COO-3077-105

Courant Institute of
Mathematical Sciences

ERDA Mathematics and Computing Laboratory

Ab Initio Effective Potentials for Atoms of the First Three Rows of the Periodic Table

Sid Topiol, Jules W. Moskowitz, Carl F. Melius,
Marshall D. Newton and Jawed Jafri

ERDA Research and Development Report

Chemistry
January 1976

New York University

ERDA Mathematics and Computing Laboratory

Courant Institute of Mathematical Sciences
New York University

Chemistry COO-3077-105

AB INITIO EFFECTIVE POTENTIALS FOR ATOMS OF THE FIRST THREE ROWS OF THE PERIODIC TABLE

Gil Topiol and Jules W. Moskowitz*
Chemistry Department
New York University, New York, New York 10003

and

Carl F. Melius
Sandia Laboratories, Livermore, California 94550

and

Marshall D. Newton and Jawad Jafri
Brookhaven National Laboratory, Upton, New York 11973

---

*Work partially supported by the ERDA Contract E(11-1)-3077.

ACKNOWLEDGMENTS

This research was performed under the auspices of the U.S. Energy Research and Development Administration (ERDA). The computations at N.Y.U. were done on the CDC 6600 and supported by ERDA under Contract E(11-1)-3077. Use of the CDC 7600's at Sandia Laboratories and Brookhaven National Laboratories was also supported by ERDA.

TABLE OF CONTENTS

page

LIST OF TABLES iv
LIST OF FIGURES vi
I. INTRODUCTION 1
II. BACKGROUND 3
  A. Pseudopotentials 3
  B. Semiempirical Effective and Model Potentials 6
  C. *Ab Initio* Effective and Model Potentials 11
III. THE CORELESS HARTREE-FOCK AB INITIO EFFECTIVE POTENTIAL 17
  A. The Coreless Hartree-Fock Orbital 17
  B. Generating the Coreless Hartree-Fock Effective Potential 23
  C. Functional Form of the Effective Potential 25
IV. RESULTS 27
  A. First Row 27
  B. Second Row 48
  C. Third Row 62
  D. Cu One Electron CHFEP 89
V. CONCLUSION 92
REFERENCES 93

LIST OF TABLES

Table		page
1	One Valence Electron Hamiltonians	8
2	Effective Potentials for Li, Be, B	33
3	" " " C, N, O	34
4	" " " F, Ne	35
5	Be Tests	36
6	B Tests	37
7	C Tests	39
8	N Tests	41
9	O Tests	43
10	F Tests	45
11	Exponents for Four Term Gaussian Basis 2s and Coreless Hartree-Fock Orbitals. Li through Ne	46
12	Small Basis Set Calculations for F and O	47
13	Effective Potentials for Na, Mg, Aℓ	51
14	" " " Si, P, S	52
15	" " " Cℓ, Ar	53
16	Mg Tests	54
17	Aℓ Tests	55
18	Si Tests	56
19	P Tests	57
20	S Tests	58
21	Cℓ Tests	59
22	Exponents for Small Gaussian Basis 3s and 3p Coreless Hartree-Fock Orbitals. Na through Ar	60

List of Tables Continued

Table page

23 Small Basis Set Calculations for S and C 61

24 Effective Potentials for K, Ca, Sc 66

25 " " " Ti, V, Cr 67

26 " " " Mn, Fe, Co 68

27 " " " Ni, Cu, Zn 69

28 Ca Tests 70

29 Sc Tests 72

30 Ti Tests 74

31 V Tests 76

32 Cr Tests 78

33 Mn Tests 80

34 Co Tests 82

35 Cu Tests 84

36 Zn Tests 85

37 Exponents for Three Term Gaussian Basis 4s Coreless Hartree-Fock Orbitals. K through Zn 87

38 Small Basis Set Calculations for Ti and Cu 88

39 Ni, Cu One Electron Effective Potentials 89

40 Cu One Electron Effective Potential Tests 90

LIST OF FIGURES

Figure page

1 Three Different Cu 4s Orbitals 20

2 Coreless Hartree-Fock and Full SCF Orbitals for F 2s, Cℓ 3s and Cℓ 3p 21

3 Coreless Hartree-Fock and Full SCF Orbitals for Ti and Cu 4s 22

4 Effective Potential and Full SCF Orbitals for F 2s 31

5 Nitrogen CHFEP's for S, P and D 32

6 Effective Potential and Full SCF Orbitals for Si 3s and Aℓ 3p 49

7 Sulfur CHFEP's for S, P and D 50

8 Effective Potential and Full SCF Orbitals for Cu 63

9 Copper CHFEP for S, P and D 64

10 CHFEP's for Ti, Mn, Ni, Cu 65

Abstract

The Coreless Hartree-Fock Effective Potential (CHFEP) method is used to replace the core orbitals for atoms of the first three rows of the periodic table. Self Consistent Field (SCF) calculations indicate that these effective potentials give Hartree-Fock quality orbitals and orbital energies. Optimized small basis sets for use with these effective potentials are presented along with some tests of these basis sets. It is seen that the effective potential allows one to use such small basis sets without the introduction of any serious error. These smaller basis set calculations allow for great savings in computational time and cost.

I. INTRODUCTION

The various electronic structure models used by chemists to help them understand and describe chemical behavior have changed very little in the more than fifty years since the formulation of the first principles of quantum mechanics. The concept of valence electrons being responsible for most of the chemical behavior that has been studied, is one which has always stayed alive and is now again coming into the foreground. How the 1s orbital of a transition metal changes when forming, say, a hydride is not a question which does, nor need concern us since we all know this change is slight. Our problem is that quantum mechanics and the principle of indistinguishable electrons has placed upon us the burden of having to include core electrons in our calculations in order to properly account for the electronic structure of atoms and molecules. In order to carry out calculations on molecular systems, using Hartree-Fock-Roothaan type equations, various highly sophisticated computer programs have been developed and refined to stages where they can handle virtually any molecular system of interest. As more complicated systems are studied, the computer time and space required to perform these calculations places an upper limit on our capabilities To overcome this problem various approximation techniques have arisen. These techniques all have a common theme: it is the valence electrons which undergo significant changes during reactions. Unfortunately it is generally found that the simpler the calculations become, the greater the loss in accuracy becomes. The present work contains a method which also leans on the concept of valence electrons, and results in a great reduction in the size and cost of calculations, but which is found not to be accompanied by a serious loss in accuracy.

II. BACKGROUND

In order to appreciate the method used here, a brief account of earlier works which led to it is presented. This review is not intended to be an historical one, nor a complete survey of all the work done to the present on pseudopotentials, effective potentials, model potentials, etc. The intention here is to present some of the results of earlier investigations into approximation techniques which in some sense led to the present scheme as both a logical and intuitive conclusion.

A. Pseudopotentials

From experimental and theoretical studies on numerous molecular systems, we know that it is the valence orbitals which are responsible for chemical bonding etc., and that it is primarily the outermost part of the valence orbital in which this takes place. It is therefore important that any method developed to predict chemical properties give an accurate description of the "tail" of the valence orbitals. The other region of the valence orbital, the "core" part, also requires careful consideration, since this is the part that must be kept out of (orthogonal to) the core orbitals in order that we arrive at physically realistic results. These two features of valence orbitals, although of the utmost importance, have an important difference. For the tail region of the orbital it is not only important that this part be accurately accounted for, but that we be able to retrieve the information that describes that region. On the other hand, for the "core" region of the valence orbital, we only require that it be handled with sufficient accuracy to prevent physically unrealistic results. This has been taken advantage of by Weeks, Hazi and Rice[1] who have given a generalization of a method due to Phillips and Kleinman[2] known as the pseudopotential method. Since the core region of the valence orbital requires extra basis functions for the reproduction of nodes and wiggles; and since there is no real interest in having an accurate description of these nodes and wiggles, their only purpose being to maintain orthogonality to the core, their method allows one to use a smooth pseudowavefunction for the valence orbital. Since it is a smooth wavefunction it requires fewer basis functions for its description, leading therefore to a simplification of the calculations. Mathematically they transform the Hamiltonian

$$H\phi_v = (T+V)\phi_v = \varepsilon_v\phi_v \tag{1a}$$

subject to

$$\langle\phi_c|\phi_v\rangle = \delta_{cv} \tag{1b}$$

to $$H^{PS}\chi_v = (T+V+V^{PS,GPK})\chi_v = \varepsilon_v\chi_v \tag{2}$$

where

$$V^{PS,GPK} = -HP - PH + PHP + \varepsilon_v P \tag{3}$$

is the "Generalized Phillips-Kleinman" pseudopotential, and

$$P = \sum_c^{\text{core}} P_c = \sum_c^{\text{core}} |c\rangle\langle c| \tag{4}$$

is the projection operator which projects onto the core orbitals. The Phillips-Kleinman form for V^{PS} is

$$V^{PS,PK} = \sum_c^{\text{core}} (\varepsilon_v - \varepsilon_c) P_c \ . \tag{5}$$

The pseudoorbital above, χ_v, need not be identical to ϕ_v. ε_v will be an upper bound to ε for any arbitrary basis set. Thus, we are at liberty to choose for χ_v some small basis set which contains only those functions required for an accurate description of the tail region. To see how ε_v is an upper bound to ε, we note that any arbitrary function χ_v can be written in terms of the complete set

$$\chi_v = \sum_c a_c \phi_c + \phi_v + \sum_e a_e \phi_e \tag{6}$$

Any component of χ_v due to the first term, has its energy lifted to ε_v by the pseudopotential which adds an amount $\varepsilon_v - \varepsilon_c$ onto ε_c (for ϕ_c) giving ε_v as its energy. The second term already has ε_v as its energy and any component of χ_v from the third term will be higher than ε_v so that any arbitrary χ_v will in fact have ε_v as an upper bound.

It should be noted that in the Hamiltonians described above, no approximations have been made, but rather a transformation from an equation (1a) subject to constraint (1b) to a new unconstrained equation (2). These are the only Hamiltonians correctly termed "Pseudohamiltonians" whereas those approximations to be presented below are "model" or "effective" Hamiltonians.

The problems with the above Hamiltonians are clear. First, if care is not taken it is possible to choose a χ_v which has very little resemblance to ϕ_v except in energy. Second, consider the ground state of Na. In order to solve for the 3s orbital above, we must know the core orbitals which we must get by a Self Consistent Field type calculation which would have given us the 3s orbital anyway. To solve for an excited state we must either recalculate the projection operators P_c or assume they have not changed, whereby the method becomes tantamount to a frozen core approximation. In addition, we are left with the undesireable coulomb and exchange integrals over the core orbitals.

B. Semiempirical Effective and Model Potentials

To help improve the situation a number of approximation techniques have been developed. For convenience Table I gives some of their Hamiltonians along with the Phillips-

Kleinman Pseudohamiltonian. Note that although some of these have been developed for many valence electron systems, only the one valence electron Hamiltonians are presented, allowing for ease of comparison. For more than one valence electron, the appropriate coulomb and exchange operators over the valence orbitals must be added.

The first class of these, the semiempirical potentials, are usually formed by adjusting the parameters to fit experimental binding energies. Although this corrects somewhat for correlation effects, there is no guarantee that accurate wavefunctions and other properties will be correctly reproduced.

Simons and Mazziotti[6] have tried using a Gaussian basis set with the Hamiltonians

$$H = T - \frac{n_v}{r} + \frac{A}{r} e^{-2kr} \tag{7}$$

and

$$H = T + C_1 r^2 + C_2 \tag{8}$$

and found them to give poor results for molecules due to a lack of symmetry (ℓ) dependence. In addition, C_2 of equation (8) does not die off as it should on say another atom. The Abarenkov and Heine[7] potential improves on this somewhat by introducing an ℓ dependence and a cutoff point, i.e.

$$H = T + \sum_{\ell=0} B_\ell P_\ell \qquad r < R_C \tag{9a}$$

TABLE I. One Valence Electron Hamiltonians

Pseudohamiltonians	Examples
$H = T - \frac{n_v}{r} + \sum_{c}^{\text{core}} (\varepsilon_v - \varepsilon_c) P_c$	Phillips-Kleinman[2]
Semi-Empirical Effective Hamiltonian	
$H = T - \frac{n_v}{r} + \frac{A}{r} e^{-2kr}$	Hellmann,[3] Gombas,[4] Szasz and McGinn,[5] Simons and Mazziotti[6]
$H = T + C_1 r^2 + C_2$	Simons and Mazziotti[6]
$H = T + \sum_{\ell=0}^{\infty} P_\ell B_\ell \quad r<R_c$ = core radius $\quad = T - \frac{n_v}{r} \quad r>R_c$	Abarenkov and Heine[7]
$H = T - \frac{n_v}{r} + \sum_{\ell} \frac{B_\ell P_\ell}{r^2}$	Simons[8], Goodfriend and Hart[9]
$H = T - \frac{n_v}{r} + \sum_{\ell} \left(\frac{A_\ell}{r}\right) e^{-\gamma_\ell r^2} \; P_\ell$	Schwartz and Switalski[11]
$H = T - \frac{n_v}{r} - \frac{A}{r} e^{-\alpha r}$ atoms, $\ell > \ell$max of core $\quad T - \sum_{\ell = 0}^{\ell\text{max of core}} P_\ell B_\ell \, e^{-\beta_\ell r}$ atoms, $\ell \leq \ell$max of core $\quad T - \sum_{\ell = 0}^{\ell\text{max of core}} P_\ell C_\ell \, e^{-\gamma_\ell r^2}$ molecules	Chang *et al.*[12]

TABLE I Continued

Ab Initio Effective Hamiltonians	Examples
$H = T - \frac{n_v}{r} - \frac{n_c}{r} e^{-\alpha r} + \sum_c (\varepsilon_v - \varepsilon_c) P_c$	Coffey *et al.*[13]
$= T - \frac{n_v}{r} + \sum_c (\varepsilon_v - \varepsilon_c) P_c$ No ϕ on same center as v	
$H = T - \frac{n_v}{r} + \sum_i^{n_a} \frac{n_v}{r} A_i e^{-\alpha_i r^2} + \sum_c P_c B_c$	Bonifacic and Huzinaga[14]
$H = T - \frac{n_v}{r} + \sum_{\ell = 0}^{\ell val} \sum_i P_\ell A_{\ell,i} / r^{n_i}$	Durand and Barthelat[15]
$H = T - \frac{n_v}{r} - \sum_{\ell = 0}^{\ell val} \sum_i P_\ell A_{\ell,i} r^{n_{\ell,i}} e^{-\alpha_{\ell,i} r^2}$	Kahn and Goddard[16] Melius[17]

$$H = T - \frac{n_v}{r} \qquad r > R_c \tag{9b}$$

where P_ℓ is the angular part of the projection operator

$$P_\ell = \sum_m |\ell m\rangle\langle \ell m| = \sum_m |Y_{\ell m}\rangle\langle Y_{\ell m}|, \tag{10}$$

and where R_c is the radius of the core orbitals, and n_v is the number of valence electrons. The Simons[8] potential

$$-\frac{n_v}{r} + \sum_{\ell=0} \frac{B_\ell P_\ell}{r^2} \tag{11}$$

dies off smoothly without requiring a cutoff, and contains an ℓ dependence of the valence orbitals. There is also an analytic expression for the energy

$$\varepsilon_v = \frac{-2Z^2}{\{2P+1[(2\ell+1)^2+8B_\ell]^{1/2}\}^2} \qquad P = 0,1,2,\ldots\ . \tag{12}$$

Goodfriend and Hart[9] have developed some of these potentials by setting P = 0 and using as a wavefunction:

$$\chi_v = \left(\frac{\varepsilon^5}{3\pi}\right)^{1/2} re^{-\varepsilon r} \tag{13}$$

where ε was obtained by fitting to the STO's of Clementi *et al.*[10] To get the nth excited state, P was then set equal to n.

Schwartz and Switalski[11] used what they call a "Gaussian Screened Coulomb Potential"

$$- \frac{n_v}{r} + \sum_{\ell} P_{\ell} \frac{A_{\ell}}{r} e^{-\gamma_{\ell} r^2} \qquad (14)$$

which introduces an ℓ dependence in a Gaussian term which allows for easier use in molecular calculations and incorporation into existing programs. They have also tested the effect of taking the original basis set from which the potential was developed and leaving out the first few core type functions.

Chang *et al.*[12] have also investigated a screened coulomb potential with a basic form given by

$$- \frac{n_v}{r} - \frac{A}{r} e^{-\alpha r}$$

For the first row they find the potential to be fairly insensitive to the value of the parameter A. As they increase the atomic number the results get poorer. For Ti for example they find that they require a polynomial expression for A. They attribute this to the greater error in the frozen core approximation for larger atoms.

C. Ab Initio Effective and Model Potentials

The second class of effective Hamiltonians consist of the theoretically based Hamiltonians, that is, those which do not make use of experimental values for parameter adjustment. The simplest one in Table I, that of Coffey *et al.*,[13]

$$H = \begin{cases} T - \frac{n_v}{r} - \frac{n_c}{r} e^{-\alpha r} + \sum_c (\varepsilon_v - \varepsilon_c) P_c & \text{(15a)} \\ T - \frac{n_v}{r} + \sum_c (\varepsilon_v - \varepsilon_c) P_c \quad \text{for both orbitals on an atom different from the potentials} & \text{(15b)} \end{cases}$$

consists essentially of the Phillips-Kleinman potential with a parameterized exponential term to replace the coulomb and exchange terms of the core orbitals. They have found this form to be basis set dependent, i.e., it must be readjusted for different basis sets. They also find that when core functions are included one pseudoorbital can collapse into the core when trying to avoid another. Thus the result of a calculation with additional functions in the core region, which should give better results (greater flexibility) gives poorer results. They also find that ε_v (in the projection operator) must be readjusted after each iteration in an SCF type calculation.

The Bonifacic-Huzinaga[14] Hamiltonian

$$H = T - \frac{n_v}{r} - \sum_i^{n_a} \frac{n_v A_i}{r} e^{-\alpha_i r^2} + \sum_c^{\text{core}} B_c P_c \qquad (16)$$

uses a series of Gaussians with adjustable exponents and coefficients, and changes the $\varepsilon_v - \varepsilon_c$ part of the Phillips-Kleinman type term to B_c (an adjustable parameter). For first row atoms, however, the B_c parameter matches $\varepsilon_v - \varepsilon_c$ very well[14] so that it might have been left at the predicted ε_v-ε_c. The potential does have the advantage of having a Gaussian form which leads to analytic multicenter integral expressions, and can thus be incorporated into existing Hartree-Fock programs (in fact the author has adjusted the programs for effective potentials described below to run with this type of a potential, but has as yet only performed some preliminary tests on them for atoms and small molecules). Bonifacic and Huzinaga have found this potential to be basis set dependent. The B_c parameter must be readjusted for different basis sets. They also find that for the first row the 11-S type Gaussian primitive functions can only be reduced to six, by using their potential, thus leaving the most important core type (large exponent) Gaussians.

All of the above cited theoretically based potentials have their ℓ dependence in the core projection term P_c. Note, however, that the effective potentials must in part replace the exchange integrals between the core and valence electrons. Thus the effective potential must contain the ℓ dependence of the valence orbital. For example, for the first row neither a 2p nor a 3d orbital has any projection on the 1s core orbital, so that in the above schemes they would feel the same potential. However, since the exchange operator depends on its operand, the 2p exchange integral has an $\ell = 1$ dependence whereas the 3d exchange integral has an $\ell = 2$ dependence.

Durand and Barthelat[15] have recently presented an effective Hamiltonian which has the proper ℓ dependence:

$$H = T - \frac{n_v}{r} + W_R \tag{16a}$$

where

$$W_R = \sum_{\ell} \sum_{n} \frac{A_{n,\ell}}{r^n} P_\ell \tag{16b}$$

or for many electrons

$$H = T - \frac{n_v}{r} + V_{\phi_v} + W_R \tag{17}$$

where V_{ϕ_v} are the appropriate coulomb and exchange terms over the valence pseudoorbitals. They generate W_r by first finding the intersection of ϕ_v with the highest core orbital of the same symmetry (R_c = point of intersection) then fitting for a χ_v by minimizing

$$\langle \chi_v - \phi_v | \chi_v - \phi_v \rangle_{R_c \to \infty} \tag{18}$$

subject to

$$\langle \chi_v | \chi_v \rangle = 1.$$

By choosing χ_v as a linear combination of Slater orbitals

$$\chi_v = \sum_{i=1}^{n} C_i S_i$$

they arrive at the system of linear equations

$$\sum_{j=1}^{n} [<S_i|S_j>_{R_c} - \lambda<S_i|S_j>]C_j = <S_i|\chi_v>_{R_c}$$

(see Appendix I for a similar derivation). To obtain their effective potential they must then determine the parameters $A_{n,\ell}$ (Eqn. 16b). This is accomplished by minimizing the norm of the operator

$$\vec{O} = \sum_{v} [(\varepsilon_v'|\chi_v'><\chi_v'|) - (\varepsilon_v|\chi_v><\chi_v|)]$$

where χ_v is the pseudoorbital from Eqn. (18) above, ε_v is the valence orbital energy from a complete SCF calculation and where ε_v' and χ_v' are the orbital energy and pseudoorbital resulting from a particular set of $A_{n,\ell}$.

As a result of their investigations of these effective potentials for the first and second row of the periodic table, they predict that to get improved accuracy they will have to replace equation (16b) with a more elaborate form.

The last Hamiltonian in Table I has the same form as will be used in this work (this will be described separately below). It was first used by Kahn and Goddard,[16] and has the desired angular momentum dependence described earlier. For one valence electron we have:

$$H = T - \frac{n_v}{r} + U^{eff} \tag{19}$$

where

$$U^{eff} = \sum_{\ell m}\sum U_{\ell}(r)\,|\ell m\rangle\langle \ell m| \tag{20a}$$

$$= U_{LMAX}(r) + \sum_{\ell = 0}^{LMAX-1} \sum_{m} (U_{\ell}(r) - U_{LMAX}(r))\,|\ell m\rangle\langle \ell m| \tag{20b}$$

They obtain the potential by solving for a G1 wavefunction (i.e. χ_v) and inverting equation (19) to find U^{eff}, that is they operate on χ_v with H and then divide by χ_v and solve for U^{eff}.

$$U^{eff} = \varepsilon_v + \frac{z}{r} + \frac{\nabla^2 \chi_v}{2\chi_v} \; . \tag{21}$$

The G1 wavefunction is used because it is nodeless and thus does not lead to singularities during the inversion.

III. THE CORELESS HARTREE FOCK AB INITIO EFFECTIVE POTENTIAL

The present method, the Coreless Hartree Fock Effective Potential (CHFEP), developed by Carl F. Melius *et al.*[17-19,29] is designed to include the important features mentioned above. This method is now presented in detail.

A. The Coreless Hartree Fock Orbital

We wish to develop a potential which will allow us to use smooth valence orbitals (therefore, fewer basis functions) for our SCF calculations. A starting point then, would be to take such a smooth orbital and find what potential is needed to generate it. This smooth orbital should be essentially identical to the original valence orbital in the tail region while at the same time be "smoothed out" in the core region. This orbital will not have the core character of the original wavefunction and for the orbitals generated here, is termed the "Coreless Hartree Fock" (CHF) orbital. (C. F. Melius *et al.*).[17-19,29] The CHF orbital is given as

$$\chi_v^{CHF} = \phi_v^{HF} + \sum_c^{n_c} a_c \phi_c^{HF} \tag{22}$$

which gives upon renormalization,

$$\chi_v^{CHF} = \sum_i^{n_c+1} \alpha_i \phi_i^{HF} \tag{23}$$

where ϕ_c^{HF} and ϕ_v^{HF} are the core and valence orbitals respectively, and n_c is the number of core orbitals. To determine χ_v^{CHF}, α_i is adjusted to give the best fit to an n = 3 Slater orbital

$$S = N_s \, r^2 \, e^{-\zeta r} \tag{24}$$

where N_s is a normalization constant. This is accomplished by minimizing the square of the difference between χ_v' and S, i.e.

$$\frac{\partial}{\partial \alpha_j} \left[\int \left(\sum_i \alpha_i \phi_i^{HF} - S \right)^2 \omega(r) r^2 \, dr \right] = 0 \tag{25}$$

with

$$\omega(r) = r^m \tag{26}$$

and where m is originally set to zero (i.e. no weight factor), and ζ in equation (24) is set at $\sqrt{-2\varepsilon_v}$, and solving for χ_v' (Reference 29). We then calculate the overlap between χ_v' and S. The process is then repeated for new values of ζ until this overlap is a maximum. With this final ζ we set

$$m = -2$$

in equation (26) and solve for χ_v^{CHF}. The final fit, therefore, has a $\frac{1}{r^2}$ weighting factor, introduced to remove the emphasis that the r = 3 Slater orbital inherently gives to the tail region. In practice this sometimes serves to remove slight nodes which may still exist, (e.g., see Figures 1, 2 and 3).

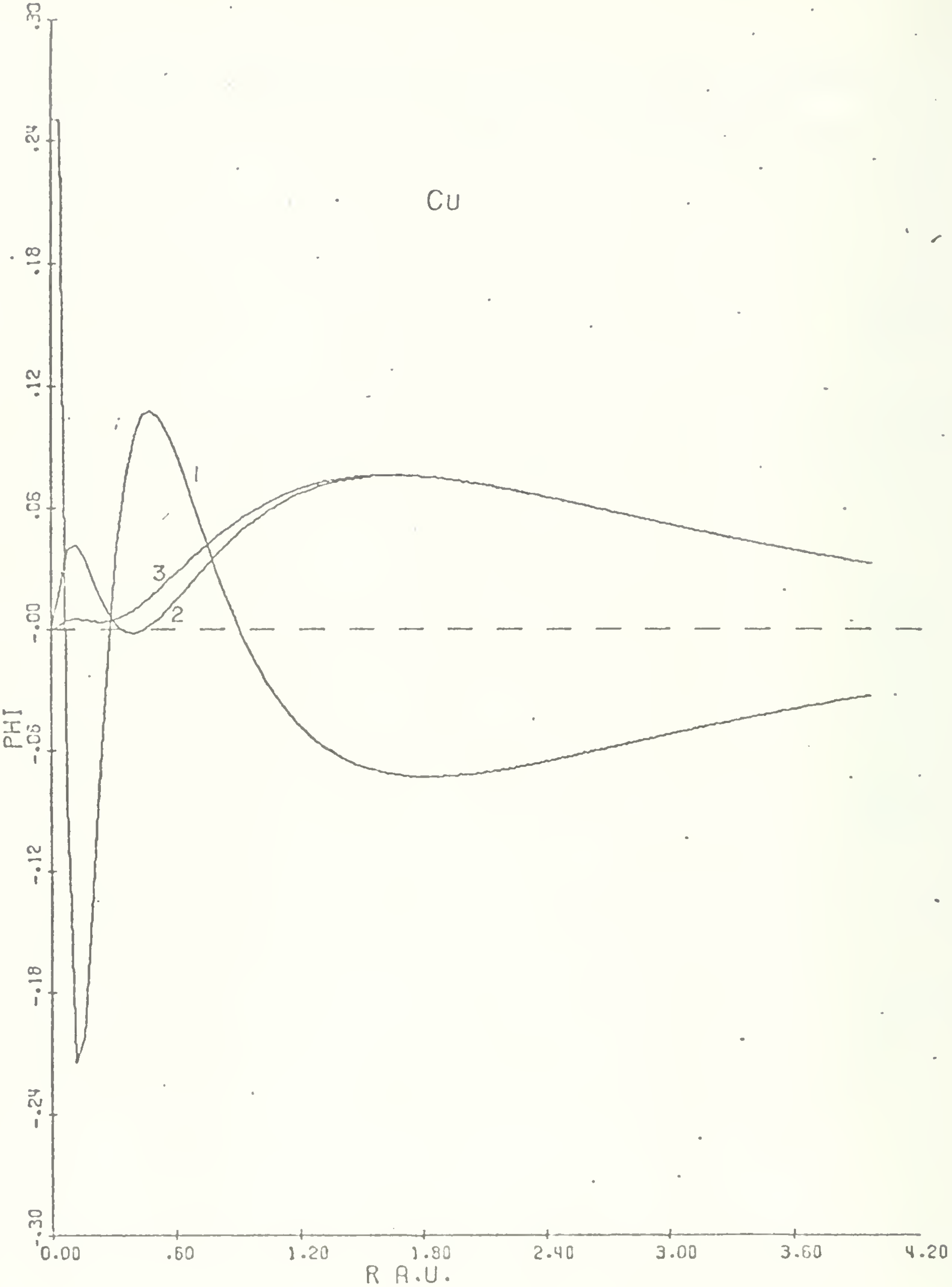


Figure 1. Three Different Cu 4s Orbitals.

Curve 1 is the 4s orbital from the full SCF calculation. Curve 2 is the Coreless Hartree-Fock orbital with the final ζ and $m = 0$ (see eqn.'s (25) and (26). Curve 3 is the final CHF orbital ($m = -2$).

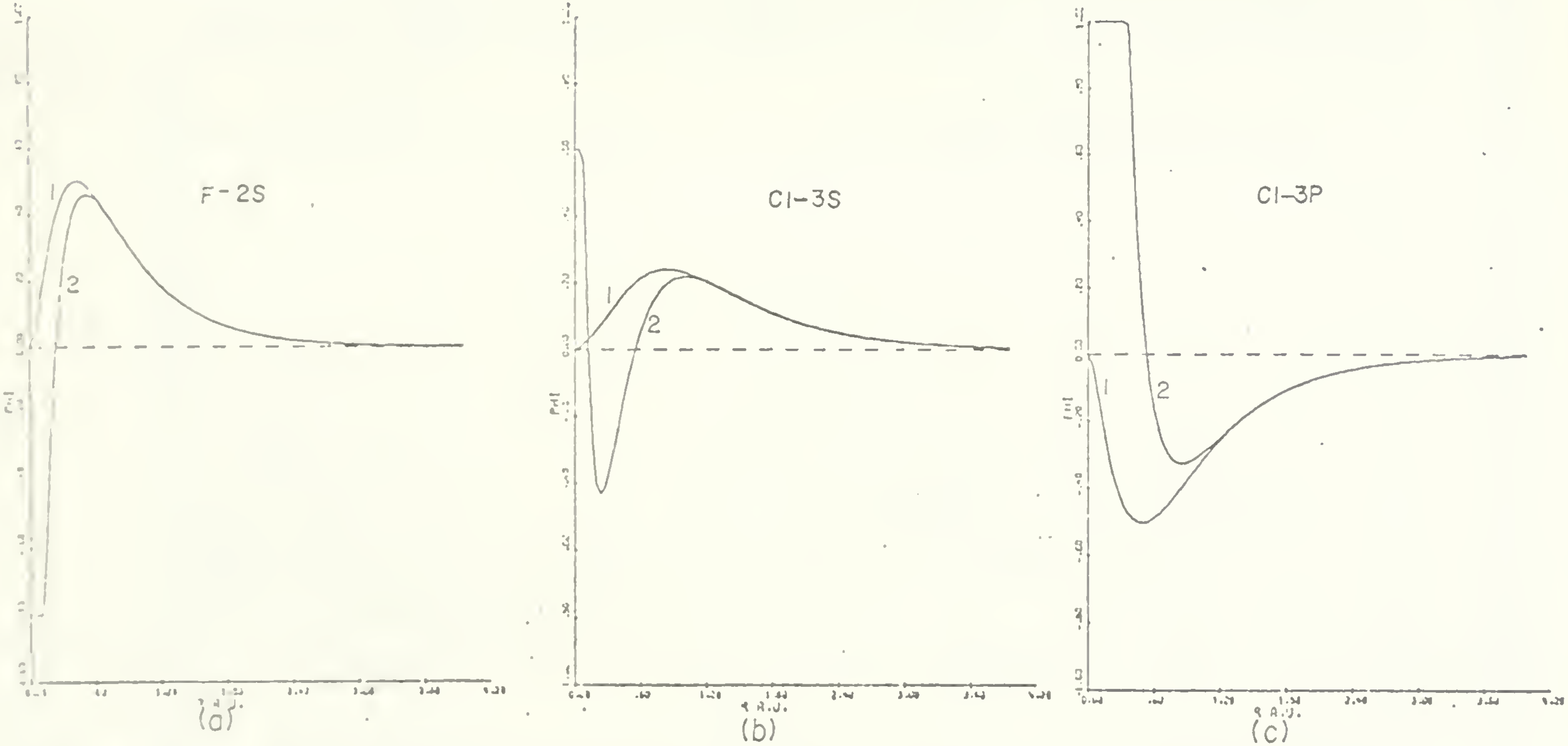
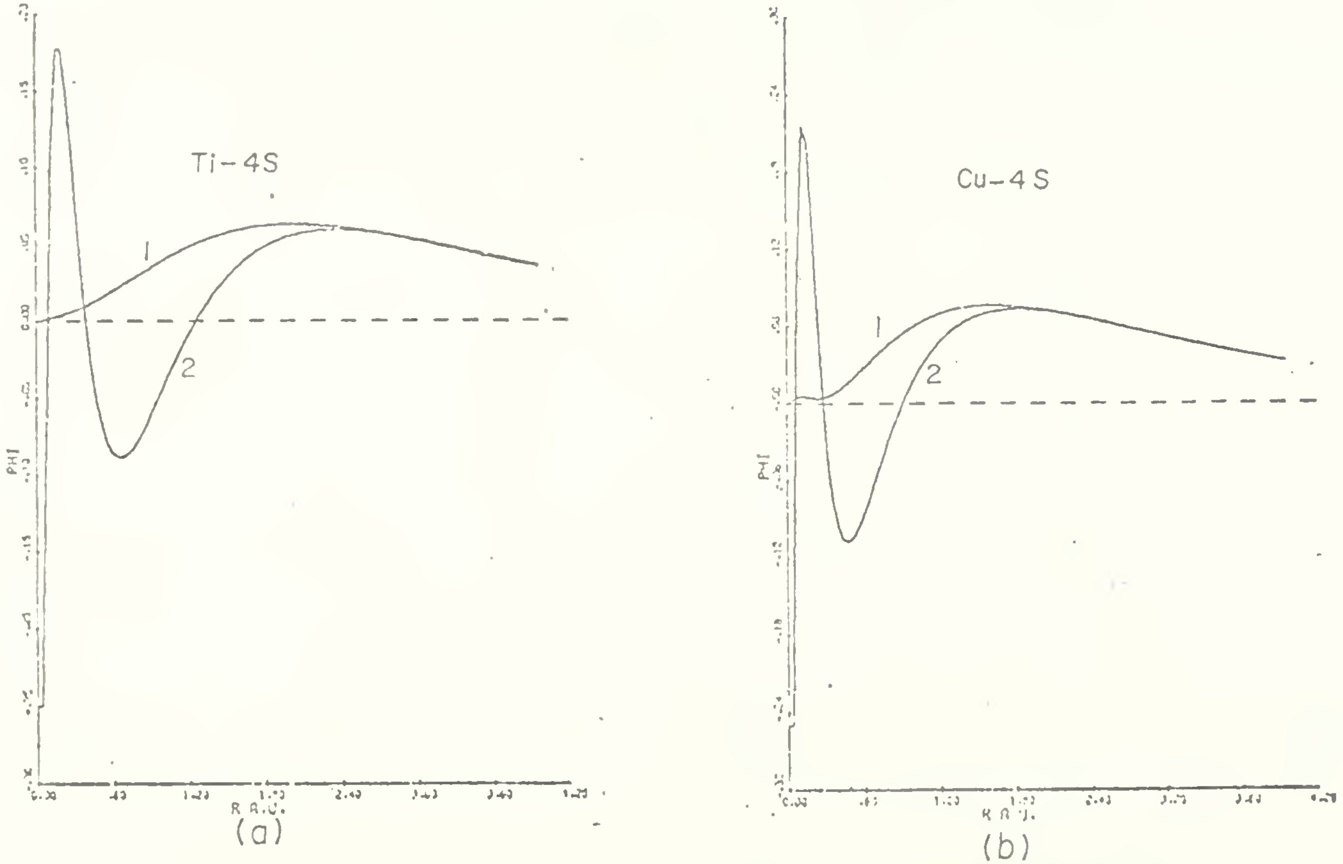


Figure 2. Coreless Hartree-Fock and Full SCF Orbitals for F 2s, Cℓ 3s and Cℓ 3p.

Curve 1 is the CHF orbital and 2 is the full SCF orbital.



(a) (b)

Figure 3. Coreless Hartree-Fock and Full SCF Orbitals for Ti 4s and Cu 4s.

Curve 1 is the CHF orbital and 2 is the full SCF orbital.

B. Generating the Coreless Hartree Fock Effective Potential

As an example of how the effective potential is then obtained, we develop here the Mn 's' effective potential. The Hartree-Fock Hamiltonian for the 4s orbital in Mn is

$$H^{HF}_{4s} = -\tfrac{1}{2}\nabla^2 - \frac{25}{r} + \sum_c (2J_c - K_c) + J^{HF}_{4s} + \sum_{m_\ell=-2}^{2} (J_{3d,m_\ell} - \tfrac{1}{2}K_{3d,m_\ell}) \quad (28)$$

which we replace with

$$H^{CHF}_{4s} = -\tfrac{1}{2}\nabla^2 - \frac{25}{r} + U^{EP}_{4s} + J^{CHF}_{4s} + \sum_{m_\ell=-2}^{2} (J_{3d,m_\ell} - \tfrac{1}{2}K_{3d,m_\ell}) \quad (29)$$

or

$$H^{CHF}_{4s} = -\tfrac{1}{2}\nabla^2 - \frac{7}{r} + V^{EP}_{4s} + J^{CHF}_{4s} + \sum_{m_\ell=-2}^{2} (J_{3d,m_\ell} - \tfrac{1}{2}K_{3d,m_\ell}) \quad (30)$$

where

$$V^{EP}_{4s} = U^{EP}_{4s} - \frac{18}{r} \; . \quad (31)$$

Note that H^{HF}_{4s} and H^{CHF}_{4s} do not commute, that is they have different eigenfunctions (for the "4s" orbital these are ϕ^{HF}_{4s} and χ^{CHF}_{4s} respectively), and operate on slightly different spaces. Equations (28) and (30) give

$$H^{HF}_{4s}|\phi^{HF}_{4s}> = \varepsilon^{HF}_{4s}|\phi^{HF}_{4s}> \quad (32)$$

and

$$H_{4s}^{CHF}|\phi_{4s}^{CHF}> = \varepsilon_{4s}^{CHF}|\phi_{4s}^{CHF}> \qquad (33)$$

At this point V_{4s}^{EP} and ε_{4s}^{CHF} are not known, and we choose

$$\varepsilon_{4s}^{CHF} = \varepsilon_{4s}^{HF} \equiv \varepsilon_{4s} \qquad (34)$$

so that we may get essentially the same eigenvalue spectrum for H^{CHF} as for H^{HF}.

We now wish to find that V_{4s}^{EP} which will generate χ_{4s}^{CHF} and ε_{4s}. This s potential is to be used in SCF type equations where its effect will be felt through its matrix elements. Therefore an important feature of the effective potential is that it produce the proper matrix elements (rather than have a physically appealing form). Thus the best way to determine V^{CHF} is to do a matrix (in this case vector) fit over some arbitrary basis set.* Operating on equation (33) from the left with an arbitrary basis set $<i|$ we get

$$<i|H_{4s}^{CHF}|\chi_{4s}^{CHF}> = <i|\chi_{4s}^{CHF}>\varepsilon_{4s} \qquad (35)$$

which combines with equation (30) to give

$$<i|V_{4s}^{EP}|\chi_{4s}^{CHF}> = <i|\varepsilon_{4s} - (-\tfrac{1}{2}\nabla^2) - \frac{7}{r} \qquad (36)$$

$$+ J_{4s}^{CHF} - \sum_{m_\ell=-2}^{2} (J_{3d,m_\ell} - \tfrac{1}{2}K_{3d,m_\ell})|\chi_{4s}^{CHF}>$$

---

*For convenience, the arbitrary basis set chosen is that used for ϕ_{4s}^{HF} or in effect χ_{4s}^{CHF}.

C. Functional Form of the Effective Potential

The form of the effective potential used here will be

$$V^{EP} = V_{LMAX}(r) + \sum_{\ell = 0}^{LMAX-1} \sum_{m} \Delta V_{\ell}(r) |\ell m\rangle\langle \ell m| \qquad (37)$$

where

$$\Delta V_{\ell}(r) = V_{\ell}(r) - V_{LMAX}(r) \qquad (38)$$

and where $V(r)$ $(= V_{LMAX}(r)$ or $\Delta V_{\ell}(r))$ is given by

$$V(r) = \sum_{i} A_i \, r^{n_i} \, e^{-\alpha_i r^2} . \qquad (39)$$

The parameters of equation (39) (A_i, n_i and α_i) are adjusted to give the best solution to equation (36) (for the Mn s potential) for V^{EP} by performing a non-linear least squares fit. To see how this form is arrived at we note first that these effective potentials have an essentially Gaussian form (equation (39)). This will allow us to arrive at simple analytic expressions for the integrals over Gaussian basis functions, with which they will be used (see for example Reference 17 or Reference 29). There is also an ℓ dependence which is not cut off at the maximum ℓ value of the core orbitals. This satisfies the criterion described earlier for the ℓ dependence of an effective potential. We do note however, that there is a finite cut off for the ℓ value. This can best be explained with an example. For a Mn valence orbital we expect to see a very different potential for a 'd' and a 'p' electron, where for Mn, 'd' core orbitals do not exist. For an 'f' orbital we expect to see almost the same potential as for 'd' since neither of these have any core orbitals of the same symmetry, and both have very little amplitude in the core region which results in very little core dependence of the coulomb and exchange integrals that are being replaced. In general, it should suffice to set LMAX as one greater than the highest ℓ value of the core orbitals. Thus using equation (37) for Mn, orbitals with s, p and d symmetry on the effective potential center will all feel different potentials, whereas all orbitals which have a symmetry dependance on this center of higher ℓ value will feel the same potential as d.

IV. RESULTS

Using the procedure described above, Coreless Hartree-Fock Effective Potentials (CHFEP) were developed for atoms of the first three rows of the periodic table.

A. First Row

Tables 2 through 4 contain the CHFEP's for Li through Ne. Each of these contains a $-n_v/r$ term in the d part of the potential (that felt by all electrons), which just represents the nuclear attraction term of an atom with

$$Z_{total} - Z_{core} = Z_{eff} = n_v$$

electrons. In addition for C, N, O and Ne we have the two terms:

$$-\frac{1.6}{r} e^{-80.0r^2} , \quad -\frac{0.4}{r} e^{-30.0r^2} .$$

These terms were preset at these values. Together they go to $-2/r$ ($= -n_c/r$) as r goes to zero, so that together with the $-n_v/r$ term above there is an overall $-z/r$ dependence of the potential as r goes to zero. This of course introduces a constraint, and to test its importance, the flourine CHFEP was generated both with and without this constraint. The difference in the two effective potential was found to be negligible. For the remaining atoms it was decided to include this constraint for aesthetic reasons as long as there was no serious difficulty fitting a potential subject to this constraint. The value of n as well as the number of terms, for the different potentials are, as described above, parameters of the potential. Where possible these were kept fairly uniform. Thus for example C, N and O are alike in number of terms and n values. For B (which was done later) it was found necessary to add 1 term and change the n values in the s-d part of the potential to get a reasonable fit. For Be one term for the p-d potential gave essentially as good a fit as two (this is primarily because the p and d electrons see essentially the same core so that V_{p-d}, representing the difference between the p and d potential is small).

To see how well these potentials perform, the ground state and various excited states were calculated both with and without these CHFEP's[21]. The results of these tests are presented in Tables 5 through 10. The basis sets used to test these were the 11S, 7P basis of S. Huzinaga and Y. Sakai[18] contracted to (5,1,1,1,1,1,1/3,1,1,1,1). In all cases the errors in the orbital energies and total energies were less than a few hundredths and a few thousandths of an a.u. respectively (or a few tenths and a few hundredths of an electron volt respectively). In most cases however, the errors were an order of magnitude better. As expected the greatest errors occur for those states which are furthest from the state from which the potential was created. Thus the errors in the energies for promoting an electron from a 2s orbital to a 2p orbital is greater for C than for Be. This is because the p part of the potential used for the carbon configuration ($2s^1 2p^1 2p^1 2p^1$), was generated from a p orbital in the ground state ($2s^2 2p^1 2p^1$), whereas for Be, in order to get the p part of the potential the p orbital of the $2s^1 2p^1$ configuration was used, so that it was generated from the identical state we are looking at ($2s^1 2p^1$). In going from C to F the errors in this type of excited state are comparable. They will however be most serious for B, C and N, where these excited states are most important in forming molecules. These errors are however small enough that no serious problems are expected.

To see how well the tail of the wave function are reproduced, Figure 4 gives ϕ_{2s}^{HF} and χ_{2s}^{CHF} for flourine. We see that the wavefunctions too are well described in the present scheme.

Finally we present in Table 11 a list of 4 term s Gaussians for use with these CHFEP's. With these new basis sets the number of functions necessary to perform the SCF calculations has been greatly reduced, resulting in major savings in computational effort. The functions given in Table 11 were obtained by non-linear-least-squares fitting four single Gaussians to χ_{2s}^{CHF} and keeping the resulting exponents. For F and O these basis sets were then tested, and the results are given in Table 12. The basis set used for these tests was the four single s Gaussians uncontracted and the 7P Gaussians of S. Huzinaga and Y. Sakai[28] contracted to (31111). The results are seen to be quite good, demonstrating that the present method does in fact accomplish its goal: simplification of SCF calculations without introduction of serious errors.

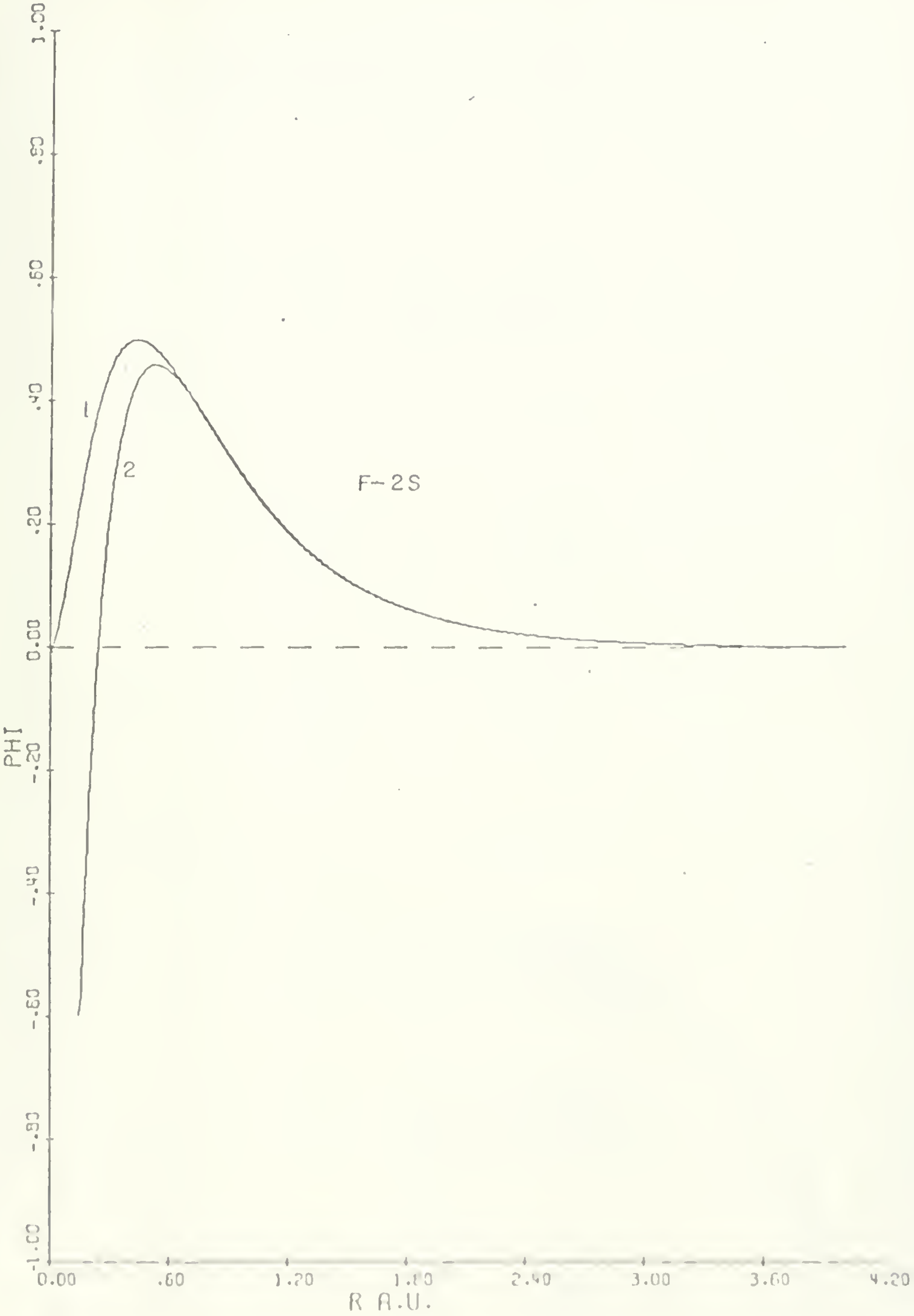


Figure 4. Effective Potential and Full SCF Orbitals for F 2s.

Curve 1 is the effective potential orbital and
2 is the full SCF orbital.

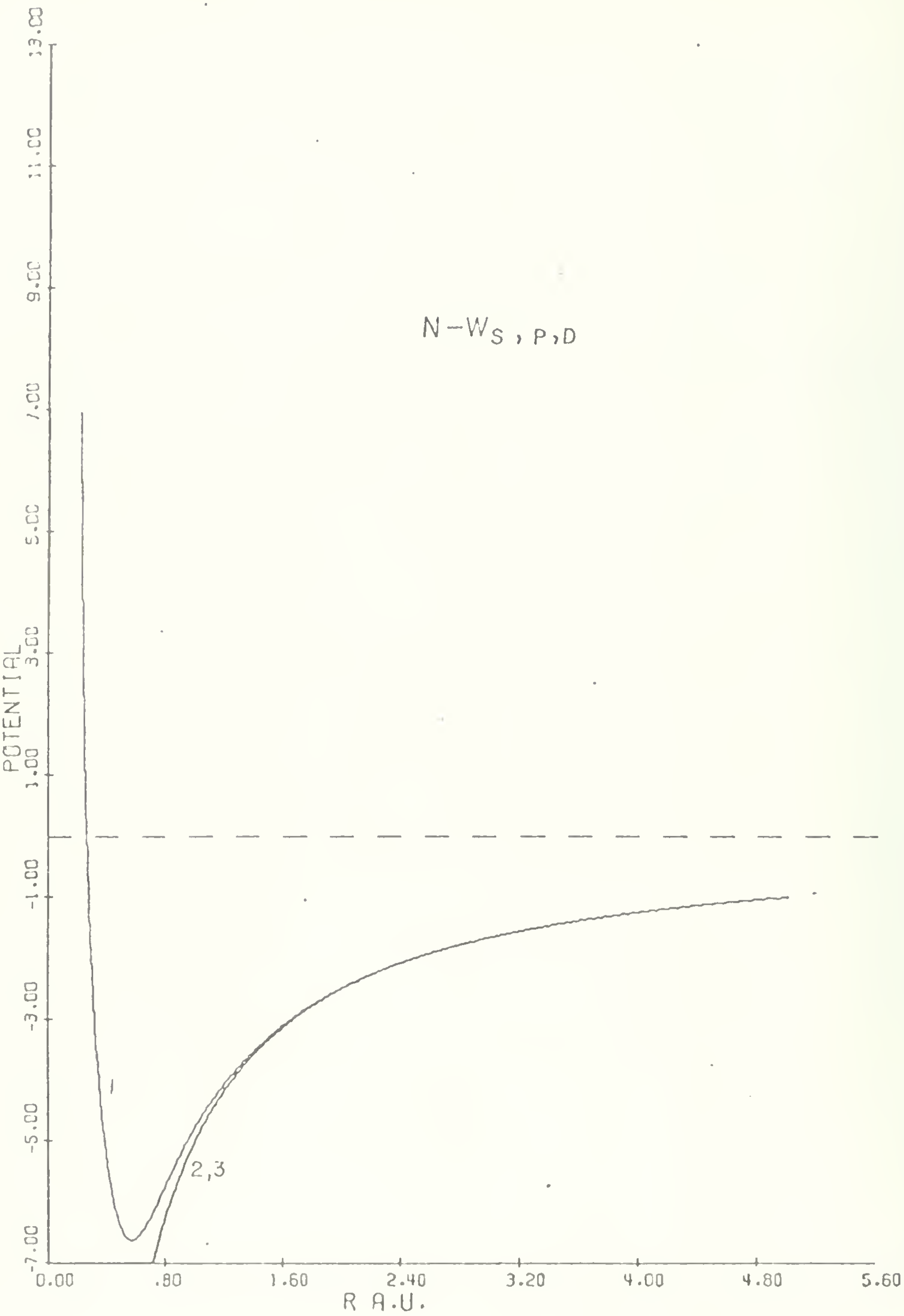


Figure 5. Nitrogen CHFEP's for S, P and D.

Curves 1, 2 and 3 are W_s, W_p and W_d respectively. ($W_s = W_{s-d} + W_d$; $W_p = W_{p-d} + W_d$).

TABLE 2. Effective Potentials for Li, Be, B[22]

	Li			Be			B		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	1.9088	2.5378	-2	0.0717	0.0756	-2	0.1042	0.0569
	0	0.9470	1.1097	-2	0.8325	1.5142	-2	1.0001	1.2199
	0	0.4905	0.3527	-2	6.4678	0.8281	-2	10.3354	2.2212
	0	0.0983	0.0089	-2	115.6211	0.4850	-2	175.8252	53.8510
V_{p-d}	0	1.0147	-0.1261	0	6.7254	-2.1453	0	61.1477	1760.5096
	0	13.1143	-0.1901				0	28.7587	- 209.5440
	0	3.0810	-0.2393						
V_d	-1	11.0026	0.4296	-1	1.5162	-0.4519	-1	0.2281	- 0.0252
	-1	1.5083	-2.4256	-1	0.1383	-0.0182	-1	133.2837	- 555.6629
	0	4.3868	2.0262	0	1.6555	0.4458	0	1.2231	- 0.0513
	0	1.7530	2.5342	-1	0.0	-2.0	-1	0.0	- 3.0
	0	0.7159	-0.0339						
	-1	0.0	-1.0						

TABLE 3. Effective Potentials for C, N, O.[22]

	C			N			O		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.7375	0.6381	-2	0.8722	0.5279	-2	0.9213	0.3955
	-2	135.2355	11.0092	-2	48.1739	3.5151	-2	28.6482	2.5165
	0	8.5606	20.1380	0	9.3861	20.1298	0	9.3033	17.0448
V_{p-d}	0	10.6864	- 3.2468	0	19.4884	-11.1778	0	52.3427	27.9779
	0	23.4980	0.7851	0	28.3756	12.1413	0	30.7220	-16.4963
V_d	-1	80.0	- 1.6	-1	80.0	- 1.6	-1	80.0	- 1.6
	-1	30.0	- 0.4	-1	30.0	- 0.4	-1	30.0	- 0.4
	0	0.5498	- 0.0399	0	0.7628	- 0.0499	0	1.0954	- 0.0662
	-1	0.0	- 4.0	-1	0.0	- 5.0	-1	0.0	- 6.0

TABLE 4. Effective Potentials for F, Ne.[22]

	F			Ne		
	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.8799	0.2712	-2	0.3568	0.0931
	-2	22.2159	2.2414	-2	23.7210	2.5069
	0	9.1358	14.6224	0	9.0707	15.3324
V_{p-d}	0	140.9425	-30.1942	0	27.3881	- 3.7807
	0	28.6394	- 1.8093	0	47.6678	7.6777
				0	1.1011	- 0.0454
V_d	-1	16.6952	- 0.7238	-1	80.0	- 1.6
	-1	26.2072	0.5889	-1	30.0	- 0.4
	0	1.3383	- 0.0647	0	12.573	- 0.2966
	-1	0.0	- 7.0	-1	0.0	- 8.0

TABLE 5. Be Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot	Error
Be$2s^2$	ε_{2s}	- 0.30926	-0.30931	.00006
Singlet		-14.57283	-0.96772	--
Be$2s^1 2p^1$	ε_{2s}	- 0.39369	-0.39914	.005
Triplet	ε_{2p}	- 0.24138	-0.24039	.001
	E_T	-14.51114	-0.90606	--
	ΔE_T	0.06169	0.06167	.00002
Be$2p^1 2p^1$	ε_{2p}	- 0.22060	-0.22130	.0007
Triplet	E_T	-14.33556	-0.72542	--
	ΔE_T	0.23727	0.24230	.005
Be$2p^1 2p^1$	ε_{2p}	- 0.19074	-0.19137	.0006
Singlet	E_T	-14.30149	-0.69131	--
	ΔE_T	0.27134	0.27641	.005
Be$2s^1 2p^1$	ε_{2s}	- 0.34220	-0.35595	.01
Triplet	ε_{2p}	- 0.10971	-0.10794	.002
	E_T	-14.38617	-0.78069	--
	ΔE_T	0.18666	0.18704	.0004
Be$^-$$2s$	ε_{2s}	- 0.08390	-0.08427	.0004
Doublet	ε_{2p}	0.02876	0.03064	.003
	E_T	-14.53025	-0.92340	--
	ΔE_T	0.04258	0.04433	.002
Be$^+$$2s^1$	ε_{2s}	- 0.66611	-0.67309	.006
Doublet	E_T	-14.27719	-0.67309	
	ΔE_T	0.26564	0.29463	.001
Be$2p^2$	ε_{2p}	- 0.17637	-0.17696	.0006
Singlet	E_T	-14.28492	-0.67472	--
	ΔE_T	0.28791	0.29300	.005

TABLE 6. B Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
B $2s^2 2p^1$	ε_{2s}	- 0.4947	-0.49489	.0002
Doublet	ε_{2p}	- 0.30983	-0.30921	.0006
	E_T	-24.52871	-2.55632	--
B $2s^1 2p^1 2p^1$	ε_{2s}	- 0.64227	-0.65079	.007
Quartet	ε_{2p}	- 0.35455	-0.35637	.002
	E_T	-24.45028	-2.48427	--
	ΔE_T	0.07842	0.07205	.006
B $2s^1(\alpha)2p^1(\beta)2p^1(\beta)$	ε_{2s}	- 0.20659	-0.19685	.01
Doublet	ε_{2p}	- 0.73404	-0.74593	.01
	E_T	-24.52587	-2.54111	--
	ΔE_T	0.00284	0.01521	.01
B $2s^1(\beta)2p^1(\alpha)2p^1(\beta)$	ε_{2s}	- 1.08168	-1.09611	.001
Doublet	$\varepsilon_{2p(\alpha)}$	- 0.12583	-0.12603	.0002
	$\varepsilon_{2p(\beta)}$	- 0.88616	-0.89233	.003
	E_T	-24.66901	-2.70195	--
	ΔE_T	- 0.14031	-0.14563	.005
B $2p^1 2p^1 2p^1$	ε_{2p}	- 0.32606	-0.32906	.003
Quartet	E_T	-24.12770	-2.15507	--
	ΔE_T	0.40101	0.40125	.0002
B $2p^1(\alpha)2p^1(\alpha)2p^1(\beta)$	$\varepsilon_{2p(\alpha)}$	- 0.80710	-0.80683	.0003
Doublet	$_{2p(\beta)}$	- 0.16662	-0.16941	.003
	E_T	-24.48397	-2.51029	--
	ΔE_T	0.04473	0.04603	.002
B^- $2s^2 2p^1 2p^1$	ε_{2s}	- 0.22909	-0.22853	.0006
	ε_{2p}	- 0.02062	-0.02030	.0004
	E_T	-24.51665	-2.54388	--
	ΔE_T	0.01205	0.01244	.0004

TABLE 6 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
B^+ $2s^2$	ε_{2s}	- 0.87382	-0.87545	.003
Singlet	E_T	-24.23722	-2.26568	--
	ΔE_T	0.29148	0.29064	.0009

TABLE 7. C Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
C $2s^2 2p^1 2p^1$	ε_{2s}	- 0.70560	-0.70673	.001
Triplet	ε_{2p}	- 0.43332	-0.43269	.0009
	E_T	-37.68802	-5.35552	--
C $2s^2 2p^1 2p^1$	ε_{2s}	- 0.71860	-0.71986	.001
Singlet	ε_{2p}	- 0.38129	-0.38062	.0007
	E_T	-37.63073	-5.29824	--
	ΔE_T	0.05729	0.05728	.00001
C $2s^1 2p^1 2p^1 2p^1$	ε_{2s}	- 0.94171	-0.95765	.02
Quintet	ε_{2p}	- 0.47886	-0.48102	.002
	E_T	-37.59860	-5.27826	--
	ΔE_T	0.07941	0.07726	.002
C $2s^1(\alpha) 2p^1(\beta) 2p^1(\beta) 2p^1(\beta)$	ε_{2s}	- 0.19114	-0.17866	.01
Triplet	ε_{2p}	- 1.63250	-1.65272	.02
	E_T	-38.75913	-6.40821	--
	ΔE_T	1.07101	1.05269	.02
C $2s^1(\alpha) 2p^1(\alpha) 2p^1(\alpha) 2p^1(\beta)$	ε_{2s}	- 2.02937	-2.04927	.02
Triplet	$\varepsilon_{2p(\alpha)}$	- 1.75350	-1.75835	.005
	$\varepsilon_{2p(\beta)}$	- 0.11999	-0.12063	.0006
	E_T	-38.98594	-6.66397	--
	ΔE_T	1.29792	1.30346	.01
C $2s^1(\beta) 2p^1(\alpha) 2p^1(\alpha) 2p^1(\beta)$	ε_{2s}	- 0.91148	-0.93602	.02
Singlet	$\varepsilon_{2p(\alpha)}$	- 0.65796	-0.63361	.02
	$\varepsilon_{2p(\beta)}$	- 0.80472	-0.84191	.04
	E_T	-37.97534	-5.62634	--
	ΔE_T	0.29733	0.27082	.03

TABLE 7 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
C $2s^2 2p^2$	ε_{2s}	- 0.72534	-0.72669	.001
Singlet	ε_{2p}	- 0.35659	-0.35590	.0007
	E_T	-37.60291	-5.27043	--
	ΔE_T	0.08510	0.08509	.0001
C^- $2s^2 2p^1 2p^1 2p^1$	ε_{2s}	- 0.36466	-0.36448	.0002
Quartet	E_T	-37.70653	-5.37368	--
	ΔE_T	0.01851	0.01816	.0003
C^+ $2s^2 2p^1$	ε_{2s}	- 1.15377	-1.15711	.003
Doublet	ε_{2p}	- 0.90477	-0.90311	.002
	E_T	-37.29161	-4.96001	--
	ΔE_T	0.39641	0.39551	.00009

TABLE 8. N Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
N $2s^2 2p^3$	ε_{2s}	- 0.941 2	- 0.94659	.005
Quartet	ε_{2p}	- 0.56877	- 0.56701	.002
	E_T	-54.20416	- 9.70829	--
N $2s^1 2p^2 2p^1 2p^1$	ε_{2s}	- 1.18936	- 1.21378	.02
Quartet	ε_{2p^2}	- 0.42856	- 0.42680	.002
	ε_{2p^1}	- 0.62783	- 0.63311	.005
	E_T	-53.80093	- 9.31297	--
	ΔE_T	0.40322	0.39533	.008
N $2s^2 2p(\alpha) 2p(\beta) 2p(\beta)$	ε_{2s}	- 0.90557	- 0.91092	.005
Doublet	$\varepsilon_{2p(\beta)}$	- 1.20158	- 1.19858	.003
	$\varepsilon_{2p(\alpha)}$	- 0.34477	- 0.34341	.001
	E_T	-54.71478	-10.21801	--
	ΔE_T	0.51062	0.50972	.0009
N $2s^2 2p^2 2p^1$	ε_{2s}	- 0.96604	- 0.97167	.006
Doublet	ε_{2p^2}	- 0.55789	- 0.55609	.002
	E_T	-54.06590	- 9.57019	--
	ΔE_T	0.13825	0.13810	.0002
N^- $2s^2 2p^2 2p^1 2p^1$	ε_{2s}	- 0.56260	- 0.56669	.004
Triplet	ε_{2p^2}	- 0.03122	- 0.03031	.00009
	ε_{2p^1}	- 0.14140	- 0.14040	.001
	E_T	-54.12460	- 9.62790	--
	ΔE_T	0.07955	0.08038	.0008

TABLE 8 Continued

State/Coupling				
N^+ $2s^2 2p^1 2p^1$	ε_{2p^2}	- 0.94207	-0.94861	.007
Triplet	ε_{2p^1}	- 1.07228	-1.07899	.007
	E_T	-52.67811	-8.16585	--
	ΔE_T	1.52605	1.54244	.02

TABLE 9. O Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
O $2s^2 2p^2 2p^1 2p^1$	ε_{2s}	- 1.24483	- 1.24565	.0008
Triplet	ε_{2p^2}	- 0.56519	- 0.56471	.0005
	ε_{2p^1}	- 0.70258	- 0.70205	.0005
	E_T	-74.81001	-15.75898	--
O $2s^1 2p^2 2p^2 2p^1$	ε_{2s}	- 1.44663	- 1.46498	.02
Triplet	ε_{2p^2}	- 0.46282	- 0.56336	.0006
	ε_{2p^1}	- 0.76812	- 0.77683	.009
	E_T	-74.18610	-15.14458	--
	ΔE_T	0.62383	0.61440	.009
O $2s^2 2p^2 2p^1 2p^1$	ε_{2s}	- 1.25631	- 1.25727	.0009
Singlet	ε_{2p^2}	- 0.57830	- 0.57777	.0005
	ε_{2p^1}	- 0.62321	- 0.62266	.001
	E_T	-74.72811	-15.67708	--
	ΔE_T	0.08189	0.08189	.000005
O $2s^2 2p^2 2p^2$	ε_{2s}	- 1.26232	- 1.26334	.001
Singlet	ε_{2p}	- 0.58518	- 0.58462	.005
	E_T	-74.68821	-15.63717	--
	ΔE_T	0.12180	0.12181	.000008
O^- $2s^2 2p^2 2p^2 2p^1$	ε_{2s}	- 0.79822	- 0.79725	.001
Doublet	ε_{2p^1}	- 0.09676	- 0.09642	.0003
	ε_{2p^1}	- 0.20342	- 0.20307	.0003
	E_T	-74.78535	-15.73399	--
	ΔE_T	0.02466	0.02499	.0003

Table 9. Continued

State/Coupling		Full SCF	Eff. Pot.	Error
$O^{-}2s^{2}2p^{2}2p^{2}2p^{2}$	ε_{2s}	- 0.92771	- 0.93744	.01
Doublet	ε_{2p}	- 0.11167	- 0.11254	.0009
	E_T	-74.10688	-15.06066	--
	ΔE_T	0.70313	.69832	.005
$O^{2-}2s^{2}2p^{2}2p^{2}2p^{2}$	ε_{2s}	- 0.44233	- 0.44056	.002
Singlet	ε_{2p}	0.27485	0.27519	.003
	E_T	-74.40161	-15.34991	--
	ΔE_T	0.40839	0.40907	
$O^{+}2s^{2}2p^{1}2p^{1}2p^{1}$	ε_{2s}	- 1.80072	- 1.80449	.004
Quartet	ε_{2p}	- 1.32689	- 1.32578	.001
	E_T	-74.37125	-15.32075	--
	ΔE_T	0.43875	0.43823	.0005

TABLE 10. F Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
F $2s^2sp^22p^22p^1$	ε_{2s}	- 1.57259	- 1.57138	.001
Doublet	ε_{2p^2}	- 0.70486	- 0.70450	.0004
	ε_{2p^1}	- 0.83442	- 0.83409	.0003
	E_T	-99.40858	-24.00570	--
F $2s^12p^22p^22p^2$	ε_{2s}	- 1.70537	- 1.71821	.01
Doublet	ε_{2p}	- 0.70232	- 0.70451	.002
	E_T	-98.52932	-23.13266	--
	ΔE_T	0.87926	0.87304	.006
F^- $2s^22p^22p^22p^2$	ε_{2s}	- 1.05757	- 1.05420	.003
Singlet	ε_{2p}	- 0.16622	- 0.16586	.0004
	E_T	-99.45223	-24.04886	--
	ΔE_T	- 0.04365	- 0.04317	.0005
F^+ $2s^22p^22p^12p^1$	ε_{2s}	- 2.19507	- 2.19730	.002
Triplet	ε_{2p^2}	- 1.36156	- 1.36107	.0005
	ε_{2p^1}	- 1.52948	- 1.52901	.0005
	E_T	-98.83139	-23.42901	--
	ΔE_T	0.57719	0.57669	.0005

TABLE 11. Exponents for Four Term Gaussian Basis 2s Coreless Hartree Fock Orbitals. Li through Ne.

Li	Be	B	C
2.89379	1.92463	3.48924	5.43368
0.61815	0.17264	0.32044	0.53387
0.07385	0.08894	0.11488	0.20524
0.02817	0.04000	0.07004	0.07958

N	O	F	Ne
7.81931	10.67015	13.94622	17.64863
0.77843	1.06640	1.39517	1.77051
0.29076	0.41239	0.54084	0.08912
0.11610	0.16019	0.20987	0.26649

TABLE 12. Small Basis Set Calculations for O and F, Energies in Hartrees.

State/Coupling		Large Basis	Small Basis[+]	Error
F $2s^2 2p^2 2p^2 2p^1$	ε_{2s}	- 1.57138	- 1.55748	.01
Doublet	ε_{2p^s}	- 0.70450	- 0.70720	.003
	ε_{2p^1}	- 0.83409	- 0.83691	.003
	E_T	-24.00570	-23.9775	.03
O $2s^2 2p^2 2p^1 2p^1$	ε_{2s}	- 1.24565	- 1.23333	.01
Triplet	ε_{2p^2}	- 0.56471	- 0.56762	.003
	ε_{2p^2}	- 0.70205	- 0.70514	.003
	E_T	-15.75898	-15.73372	.03

[+] Using the 4s type functions of Table II, and the 7p type function of S. Huzinaga and Y. Sakai (J. Chem. Phys. 50, 1371 (1969)) contracted (3,1,1,1,1).

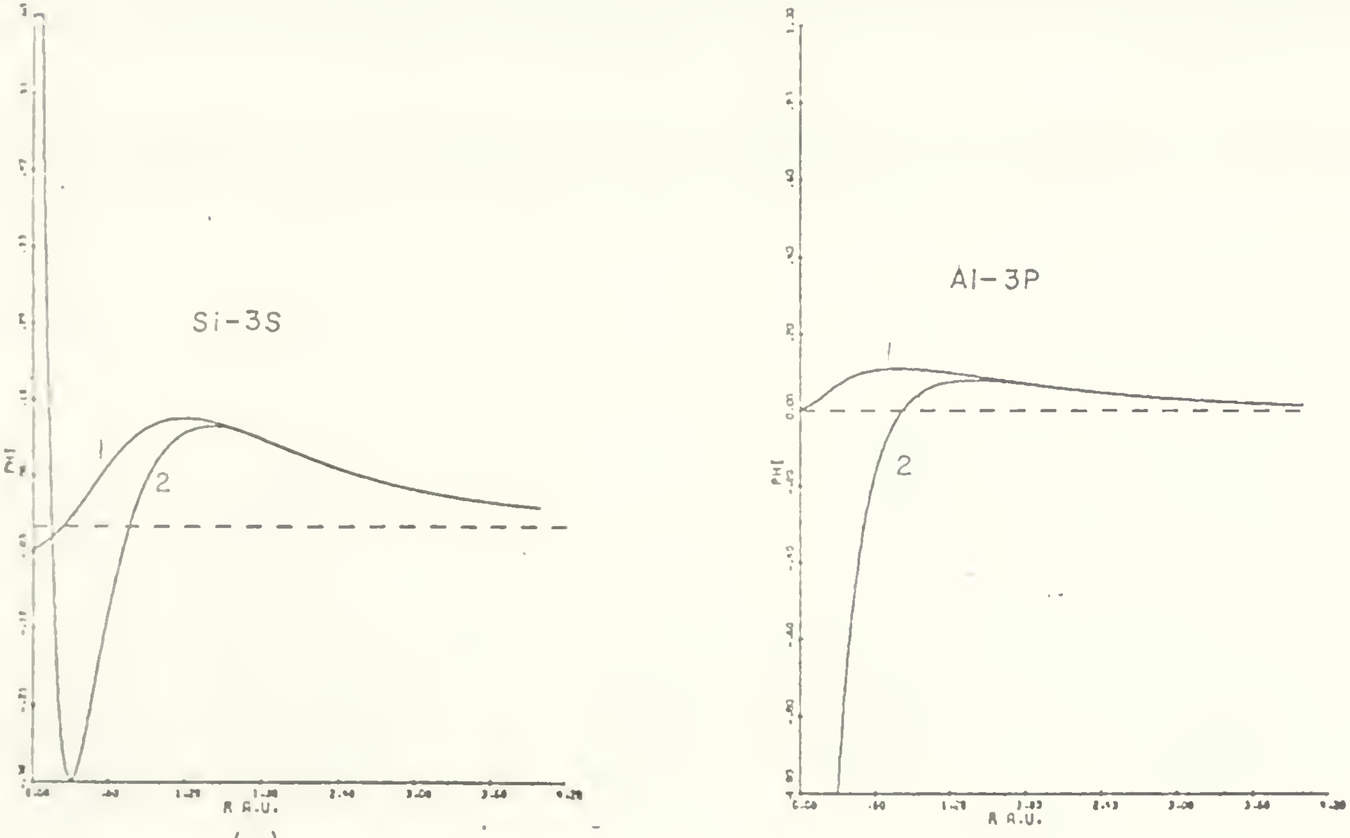
B. Second Row

The effective potentials for the second row are given in Tables 13 through 15. Analogous to the CHFEP's for the first row, most of these contain the term

$$\frac{-10}{r} e^{-80.0r^2}$$

for the $-n_c/r$ dependance. Tables 16 - 21 contain the results of the tests for this row. The results are comparable to those of the first row. Since d type polarization functions are important for the second row, we also present some tests for states where there is an occupied d orbital. Figures 6a and 6b show how the CHF 3s and 3p orbitals for Si and Aℓ compare to the Hartree Fock 3s and 3p orbitals. The s and p basis sets used for these tests was the 12s, 9p sets of Dunning[23] contracted (2,1,1,1,1,1,1,1,1,1,1/2,1,1,1,1,1,1,1).

Also given in Table 22 are the basis sets for s and p orbitals for use with effective potentials. Table 23 gives the results of tests with these small basis sets for S and Cℓ.



(a)

(b)

Figure 6. Effective Potential and Full SCF Orbitals for Si 3s and Aℓ 3p.

Curve 1 is the effective potential orbital and 2 the full SCF orbital.

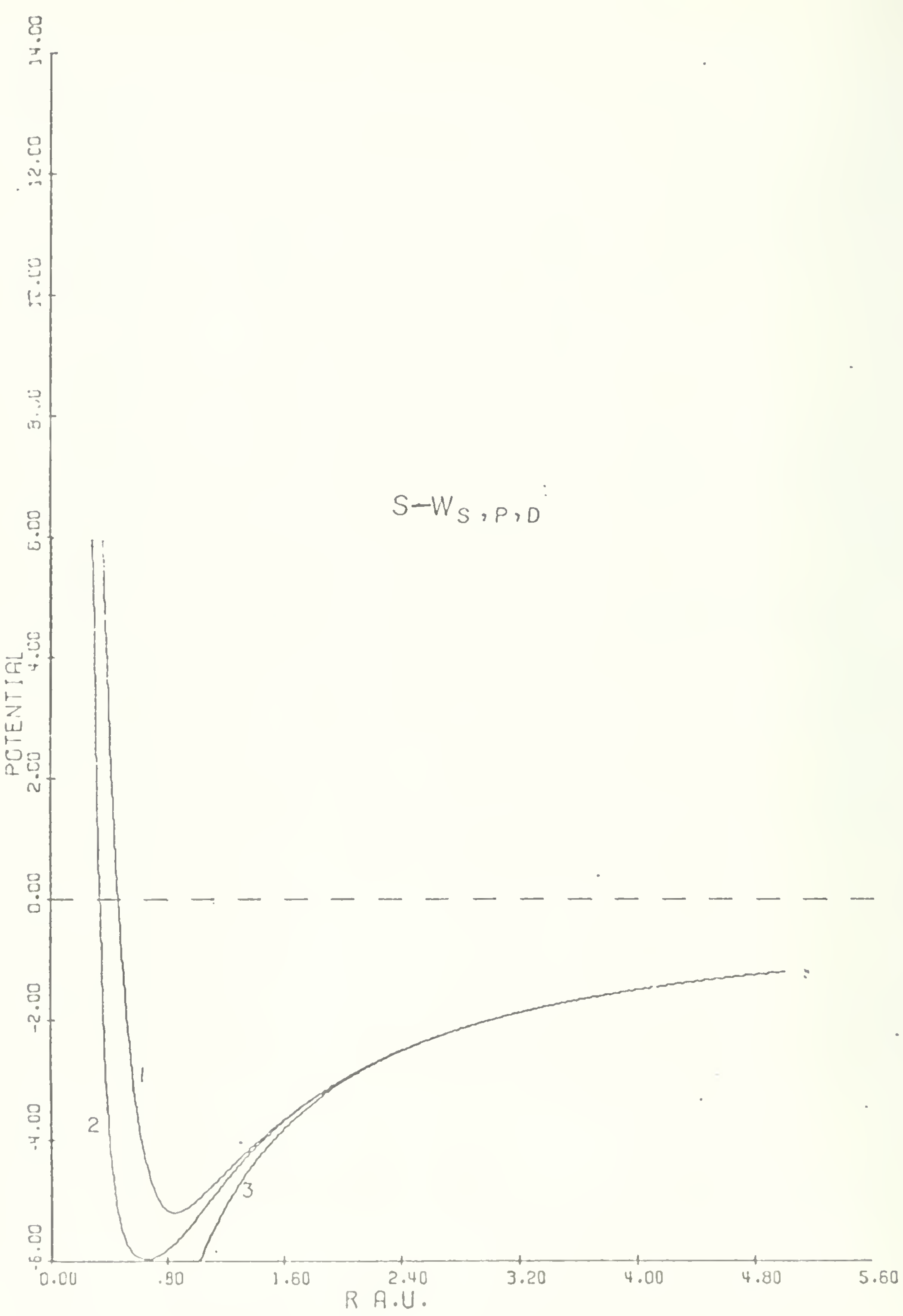


Figure 7. Sulfur CHFEP's for S, P and D.

Curves 1, 2 and 3 are W_s, W_p and W_d respectively ($W_s = W_{s-d} + W_d$; $W_p = W_{p-d} + W_d$).

TABLE 13. Effective Potentials for Na, Mg, Aℓ[22].

	Na			Mg			Aℓ		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	0	0.07621	0.00667	-2	12.46587	3.70121	-2	4.81203	0.02184
	0	0.61048	1.55413	-2	0.38043	2.08468	-2	0.47016	2.36076
	0	28.41996	29.44184	0	0.88231	23.97665	0	4.76116	23.44835
	-2	1.39397	5.85391						
V_{p-d}	0	0.30307	0.35816	-2	0.09459	0.24107	-2	0.25334	0.76255
	0	1.51658	16.14392	-2	0.65476	3.29415	-2	1.09560	2.70186
	0	2.86305	87.56787	0	1.70980	- 1.73383	0	2.44665	- 1.00971
	-2	1.77043	-46.90691						
	-2	3.92637	51.56531						
V_d	0	0.22799	- 0.02200	-1	80.0	-10.0	-1	80.0	-10.0
	0	1.79722	10.23691	0	0.02871	- 0.00020	0	0.05405	- 0.00082
	0	4.20085	9.30933	0	0.23747	- 0.04612	0	0.36484	- 0.10657
	-1	1.38587	-11.09514	0	2.92415	-10.54764	0	3.87153	-11.90555
	-1	12.22448	1.10039	-1	0.0	- 2.0	-1	0.0	- 3.0
	-1	0.0	- 1.0						

TABLE 14. Effective Potentials for Si, P, S[22]

	Si			P			S		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	12.49710	- 0.43633	-2	29.69834	- 0.79235	-2	11.91332	0.54515
	-2	0.58244	2.54384	-2	0.57358	2.07657	0	0.64895	2.10158
	0	5.80343	25.82973	0	5.94745	31.701630	0	6.85168	32.66586
V_{p-d}	-2	0.40235	0.97766	-2	0.51860	1.48015	-2	0.54502	1.30839
	-2	1.99278	2.63443	-2	3.29968	1.80076	-2	9.16701	2.54572
	0	0.81559	0.35334	0	4.70441	4.44780	0	5.02390	11.39254
V_d	-1	80.0	-10.0	-1	80.0	-10.0	-1	80.0	-10.0
	0	0.03010	- 0.00071	0	0.04923	- 0.00134	0	0.14737	- 0.01717
	0	0.36711	- 0.10869	0	0.35837	- 0.11401	0	0.62221	- 0.21571
	0	4.72826	-12.76985	0	5.71659	-13.32790	0	8.62180	-19.07242
	-1	0.0	- 4.0	-1	0.0	- 5.0	-1	0.0	- 6.0

TABLE 15. Effective Potentials for Cℓ, Ar[22]

	Cℓ			Ar		
	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.76570	2.22880	-2	0.98704	2.47706
	-2	7.97432	0.27224	-2	9.02932	0.65090
	0	7.98769	34.73881	0	9.04245	33.11992
V_{p-d}	-2	15.39029	2.68819	-2	0.97119	1.76761
	-2	0.71043	1.51527	-2	27.39315	3.22215
	0	6.94695	16.81024	0	8.81586	20.85234
V_d	-1	80.0	-10.0	-1	80.0	-10.0
	0	0.17448	- 0.02882	0	0.30076	- 0.06213
	0	0.96382	- 0.38005	0	1.82464	- 0.71798
	0	11.17574	-22.54469	0	12.26913	-19.56292
	-1	0.0	- 7.0	-1	0.0	- 8.0

TABLE 16. Mg Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Mg $3s^2$	ε_{3s}	- 0.25301	-0.25301	.000005
Singlet	E_T	-199.60837	-0.78939	--
Mg $3s^1 3p^1$	ε_{3s}	- 0.33991	-0.34236	.002
Triplet	ε_{3p}	- 0.17939	-0.17940	.00001
	E_T	-199.54013	-0.72199	--
	ΔE_T	0.06824	0.06740	.0008
Mg^+ $3s^1$	ε_{3s}	- 0.54145	-0.54747	.006
Doublet	E_T	-199.36545	-0.54747	--
	ΔE_T	0.24292	0.24192	.001
Mg^- $3s^2 3p^1$	ε_{3s}	- 0.10587	-0.10685	.0007
Doublet	ε_{3p}	+ 0.02276	+0.02359	.0008
	E_T	-199.58372	-0.76396	--
	ΔE_T	0.02465	0.02543	.0008
Mg $3s^1 3d^1$*	ε_{3s}	- 0.41993	-0.42617	.006
Triplet	ε_{3d}	- 0.05861	-0.05854	.0007
	E_T	-199.24524	-0.60593	--
	ΔE_T	0.36312	0.18346	.2

*This state was done with a less flexible basis set, and comparisons of excitation energies are not strictly valid.

TABLE 17. Aℓ Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot	Error
Aℓ $3s^2 3p^1$	ε_{3s}	- 0.39311	-0.39254	.0006
Doublet	ε_{2p}	- 0.20982	-0.21078	.001
	E_T	-241.87124	-1.89695	--
Aℓ $3s^1 3p^1 3p^1$	ε_{3s}	- 0.51931	-0.52255	.003
Quartet	ε_{2p}	- 0.26011	-0.26139	.001
	E_T	-241.78531	-1.81594	--
	ΔE_T	0.08593	0.08101	.005
Aℓ$^+$ $3s^2$	ε_{3s}	- 0.65222	-0.65592	.004
Singlet	E_T	-241.66905	-1.69448	--
	ΔE_T	0.20219	0.20247	.0003
Aℓ$^-$ $3s^2 3p^1 3p^1$	ε_{3s}	- 0.18461	-0.18350	.001
Triplet	ε_{3p}	- 0.00810	-0.00719	.0009
	E_T	-241.86649	-1.89044	--
	ΔE_T	0.00475	0.00650	.002
Aℓ $3s^2 3d^1$*	ε_{3s}	- 0.53057	-0.53413	.004
Doublet	ε_{3d}	- 0.05804	-0.05806	.00001
	E_T	-241.72705	-1.75251	--
	ΔE_T	0.14419	.14443	.0002

*See footnote of Table 16.

TABLE 18. Si Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Si $3s^2 3p^1 3p^1$	ε_{3s}	- 0.53931	-0.53855	.0008
Triplet	ε_{3p}	- 0.29672	-0.29791	.001
	E_T	-288.84865	-3.72568	
Si $3s^1 3p^1 3p^1 3p^1$	ε_{3s}	- 0.72274	-0.72858	.006
Quintet	ε_{3p}	- 0.34823	-0.34948	.001
	E_T	-288.75710	-3.64229	--
	ΔE_T	0.09155	0.08339	.008
Si$^+$ $3s^2 3p^1$	ε_{3s}	- 0.83851	-0.84257	.004
Doublet	ε_{3p}	- 0.58617	-0.59277	.007
	E_T	-288.56722	-3.44441	--
	ΔE_T	0.28143	0.28127	.0001
Si$^-$ $3s^2 3p^1 3p^1 3p^1$	ε_{3s}	- 0.28322	-0.28111	.002
Quartet	ε_{2p}	- 0.04916	-0.04788	.001
	E_T	-288.87772	-3.75195	--
	ΔE_T	0.029075	0.02628	.003
Si $3s^2 3p^1 3d^1$*	ε_{3s}	- 0.70551	-0.70972	.004
Triplet	ε_{3p}	- 0.45567	-0.46223	.007
	ε_{3d}	- 0.06125	-0.06120	.00005
	E_T	-288.62835	-3.50549	--
	ΔE_T	0.22030	0.22018	.0001

*See footnote of Table 16.

TABLE 19. P Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
P $3s^2 3p^1 3p^1 3p^1$	ε_{3s}	- 0.69511	-0.69522	.0001
Quartet	ε_{3p}	- 0.39088	-0.39127	.0004
	E_T	-340.64863	-6.45646	--
P $3s^1 3p^2 3p^1 3p^1$	ε_{3s}	- 0.87855	-0.88937	.01
Quartet	ε_{3p^2}	- 0.31316	-0.31064	.002
	ε_{3p^1}	- 0.44265	-0.44635	.004
	E_T	-340.35046	-6.16225	--
	ΔE_T?	0.29817	0.29421	.004
P^+ $3s^2 3p^1 3p^1$	ε_{3s}	- 1.03358	-1.03945	.006
Triplet	ε_{3p}	- 0.72032	-0.72659	.006
	E_T	-340.27978	-6.08914	--
	ΔE_T	0.36885	0.36732	.002
P^- $3s^2 3p^2 3p^1 3p^1$	ε_{3s}	- 0.41384	-0.41353	.0003
	ε_{3p^2}	- 0.02644	-0.02324	.003
	ε_{3p^1}	- 0.09425	-0.09292	.001
	E_T	-340.62092	-6.42278	--
	ΔE_T	0.02771	0.03369	.006
P $3s^2 3p^1 3p^1 3d^{1*}$	ε_{3s}	- 0.88540	-0.89206	.006
	ε_{3p}	- 0.57482	-0.58153	.007
	ε_{3d}	- 0.06315	-0.06301	.0001
	E_T	-340.33678	-6.15178	--
	ΔE_T	0.31186	0.30468	.007

*See footnote of Table 16.

TABLE 20. S Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
S $3s^2 3p^2 3p^1 3p^1$	ε_{3s}	- 0.87889	- 0.87731	.002
Triplet	ε_{3p^2}	- 0.39506	- 0.39396	.001
	ε_{3p^1}	- 0.47995	- 0.48277	.003
	E_T	-397.49870	-10.14770	--
S $3s^1 3p^2 3p^2 3p^1$	ε_{3s}	- 1.02846	- 1.03734	.009
	ε_{3p^2}	- 0.40457	- 0.40380	.0008
	ε_{3p^1}	- 0.53564	- 0.54272	.007
	E_T	-397.07404	- 9.72847	--
	ΔE_T	0.42466	0.41923	.005
S^+ $3s^2 3p^1 3p^1 3p^1$	ε_{3s}	- 1.24043	- 1.24418	.0001
Quartet	ε_{3p}	- 0.86231	- 0.87228	.01
	E_T	-397.16563	- 9.82035	--
	ΔE_T	0.33307	0.32735	.006
S^- $3s^2 3p^2 3p^2 3p^1$	ε_{3s}	- 0.55877	- 0.55544	.003
Doublet	ε_{3p^2}	- 0.07730	- 0.07408	.003
	ε_{3p^1}	- 0.14242	- 0.14179	.0006
	E_T	-397.52367	-10.16538	--
	ΔE_T	0.02497	0.01769	.007
S $3s^2 3p^1 3p^1 3p^1 3d^1$*	ε_{3s}	- 1.07332	- 1.08024	.007
Quintet	ε_{3p}	- 0.69951	- 0.71205	.01
	ε_{3d}	- 0.06519	- 0.06460	.0006
	E_T	-397.23034	- 9.88452	--
	ΔE_T	0.26836	0.26315	.005

*See footnote of Table 16.

TABLE 21. Cℓ Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Cℓ $3s^2 3p^2 3p^2 3p^1$	ε_{3s}	- 1.07195	- 1.07169	.0003
Doublet	ε_{3p^2}	- 0.49011	- 0.48954	.0006
	ε_{3p^1}	- 0.56893	- 0.57240	.004
	E_T	-459.47461	-15.05678	--
Cℓ $3s^1 3p^2 3p^2 3p^2$	ε_{3s}	- 1.17465	- 1.18327	.009
Doublet	ε_{3p}	- 0.49983	- 0.50036	.0005
	E_T	-458.90887	-14.49352	--
	ΔE_T	0.56584	0.56327	.003
Cℓ$^-$ $3s^2 3p^2 3p^2 3p^2$	ε_{3s}	- 0.71349	- 0.71031	.003
Singlet	ε_{3p}	- 0.13271	- 0.12919	.004
	E_T	-459.56088	-15.13495	--
	ΔE_T	0.08628	0.07816	.008
Cℓ$^+$ $3s^2 3p^2 3p^1 3p^1$	ε_{3s}	- 1.47059	- 1.47702	.006
Triplet	ε_{3p^2}	- 0.88979	- 0.89556	.006
	ε_{3p^1}	- 0.99056	- 1.00222	.01
	E_T	-459.04087	-14.62866	--
	ΔE_T	0.43384	0.42812	.006
Cℓ $3s^2 3p^2 3p^1 3p^1 3d^1$*	ε_{3s}	- 1.29997	- 1.30967	.01
Quartet	ε_{3p^2}	- 0.72284	- 0.73166	.009
	ε_{3p^1}	- 0.82421	- 0.83859	.01
	ε_{3d^1}	- 0.06560	- 0.06505	.0005
	E_T	-459.10603	-14.69335	--
	ΔE_T	0.36857	0.36344	.005

*See footnote of Table 16.

TABLE 22. Exponents for Small Gaussian Basis 3s and 3p Coreless Hartree-Fock Orbitals. Na through Ar.

Na		Mg	
S	P	S	P
0.66980	1.48524	1.10749	3.13346
0.05367	0.07059	0.08280	0.14422
0.02222	0.02231	0.01634	0.03650

Aℓ		Si	
S	P	S	P
1.53072	4.58868	2.01139	6.17212
0.13398	0.26631	0.19160	0.40375
0.01467	0.08118	0.04268	0.14448
	0.04543		0.04925

P		S	
S	P	S	P
2.48699	7.87999	3.09265	9.44112
0.26676	0.54427	0.34139	0.81239
0.08681	0.19410	0.11756	0.35676
	0.06181		0.12452

Cℓ		Ar	
S	P	S	P
3.75346	11.67869	4.29636	13.45368
0.41679	0.91292	0.52294	1.18909
0.14008	0.33878	0.18569	0.48157
	0.12138		0.16908

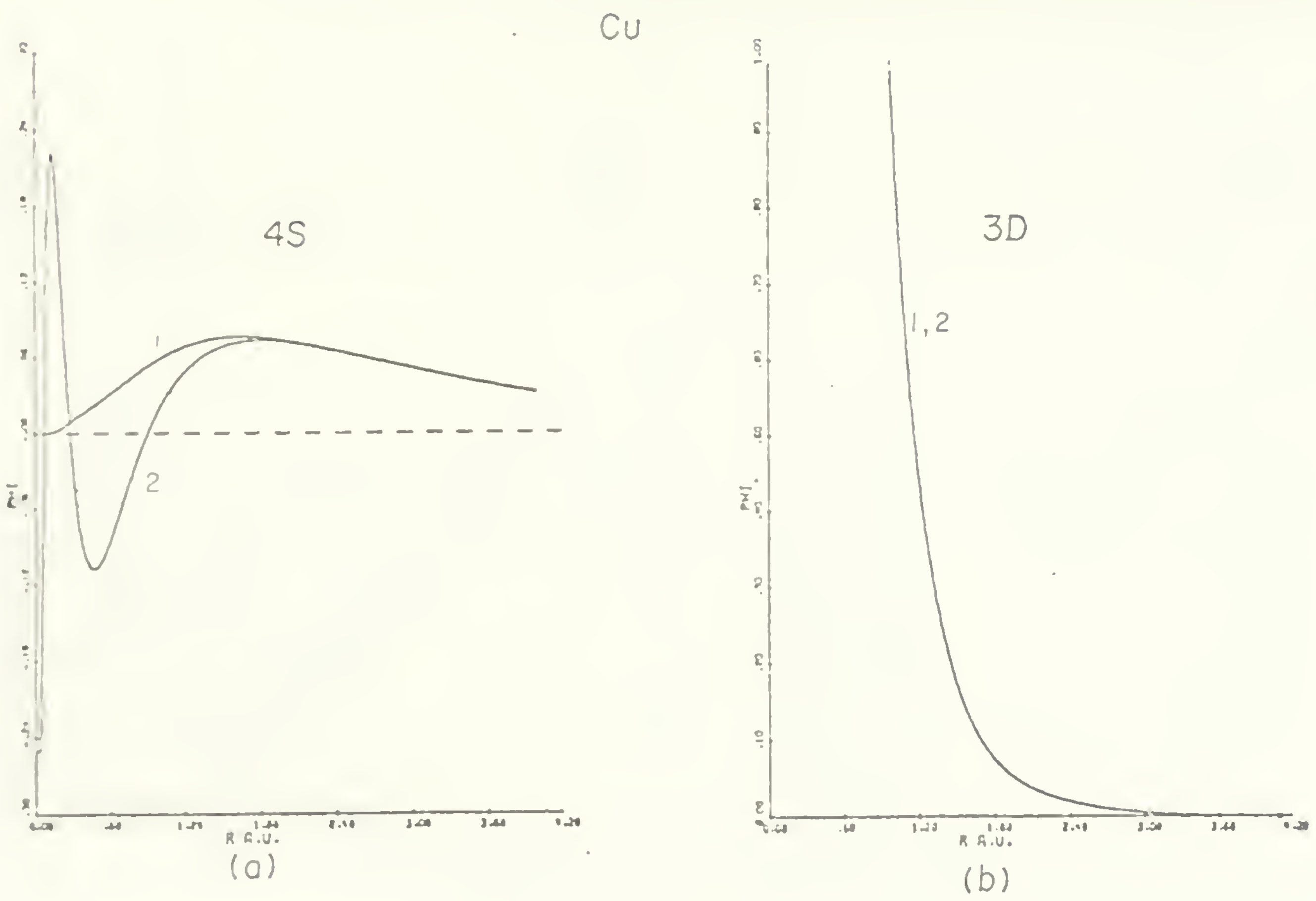
TABLE 23. Small Basis Set Calculations for S and Cℓ[+], Energies in Hartrees.

State/Coupling		Large Basis	Small Basis	Error
S $3s^2 3p^2 3p^1 3p^1$	ε_{3s}	- 0.87731	- 0.87602	.001
Triplet	ε_{3p^2}	- 0.39396	- 0.39334	.0006
	ε_{3p^1}	- 0.48277	- 0.48172	.001
	E_T	-10.14770	-10.14448	.003
Cℓ $3s^2 3p^2 3p^2 3p^1$	ε_{3s}	- 1.07169	- 1.07171	.00002
	ε_{3p^2}	- 0.48954	- 0.49014	.0006
	ε_{3p^1}	- 0.57240	- 0.57303	.0006
	E_T	-15.05678	-15.05286	.004

[+] The basis sets are those given in Table 22.

C. Third Row

Tables 24-27 give the effective potentials for K through Zn. Here it was found easier to fit the potentials without the $(-n_c/r)e^{-r^2}$ term. The results of the tests given in Tables 28 - 36 are again comparable to the first and second rows. The basis sets used for these tests was Wachters'[24] 14s, 9p, 5d contracted (6,1,1,1,1,1,1,1,1/5,1,1,1,1/4,1). For states where the 4p orbitals were occupied, we used Wachters' two extra 4p type functions. Again we present basis sets for s function in this row in Table 37. These have been tested for Cu and Ti and the results of these tests are given in Table 38. For the tests of these functions we have used the 3-s functions given in Table 37 along with Wachters'[24] 5-d functions and contracted them (1,1,1/5).



(a)

(b)

Figure 8. Effective Potential and Full SCF Orbitals for Cu.

Curve 1 is the effective potential orbital and 2 the full SCF orbital.

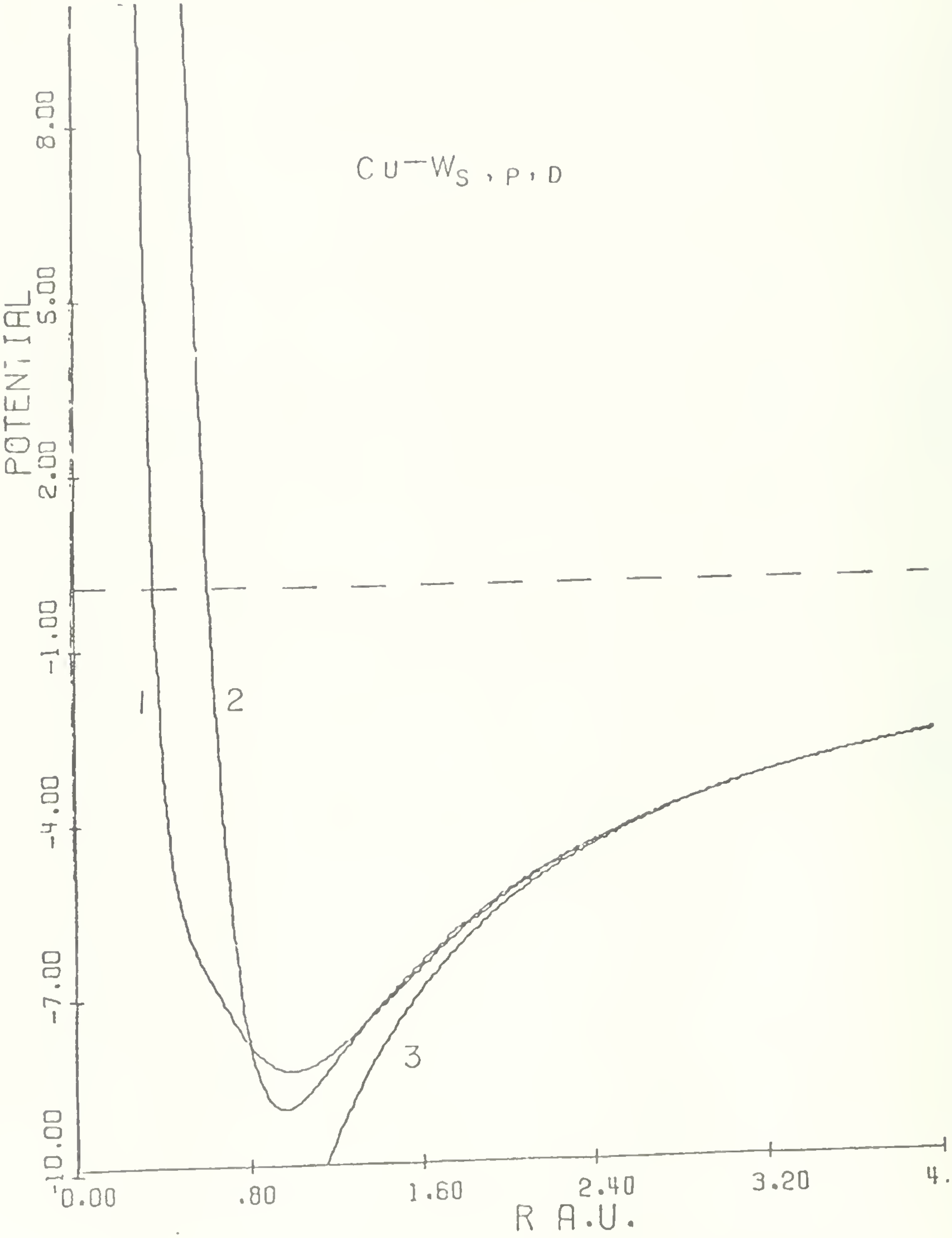
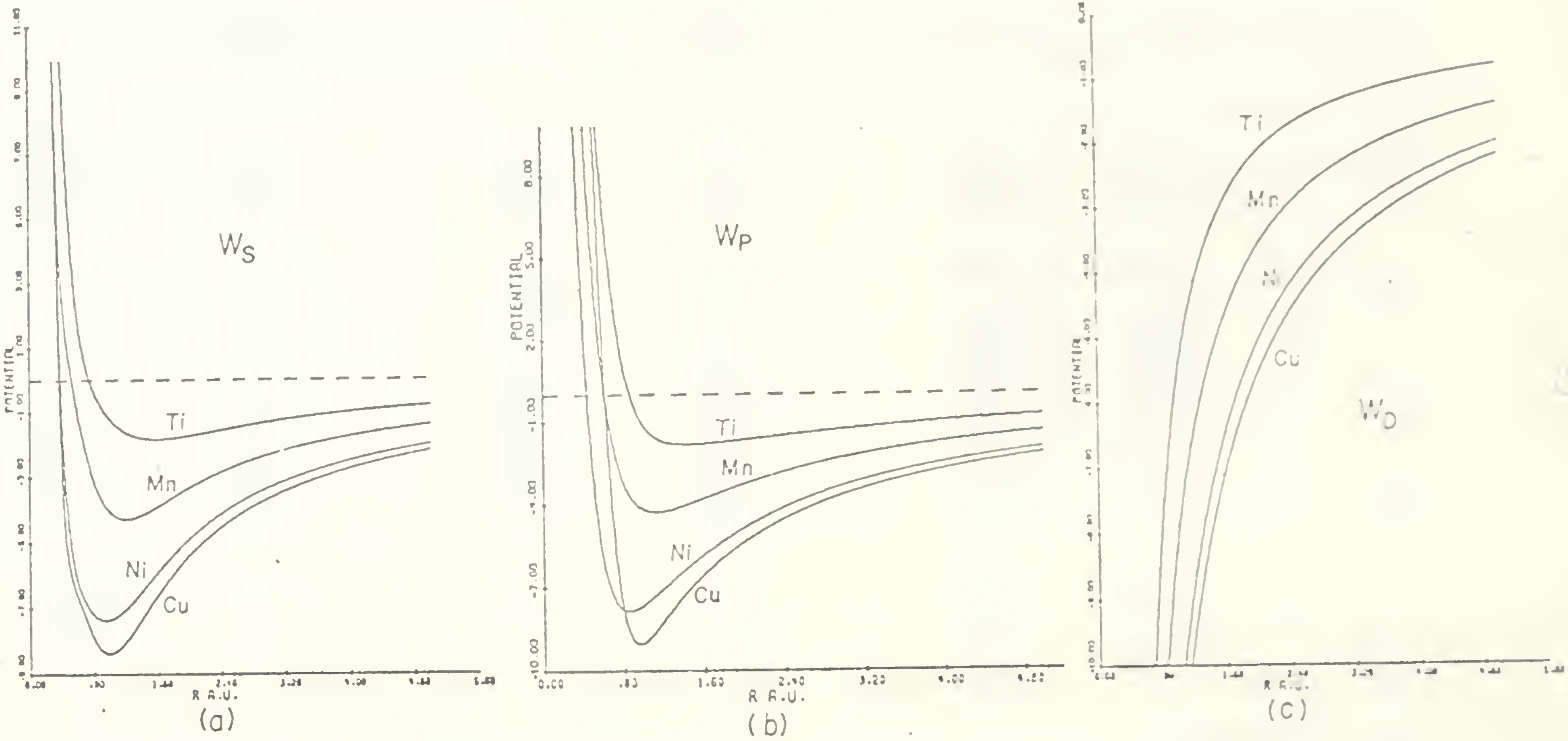


Figure 9. Copper CHFEP's for S, P and D.

Curves 1, 2 and 3 are W_s, W_p and W_d respectively. ($W_s = W_{s-d} + W_d$; $W_p = W_{p-d} + W_d$).



(a) (b) (c)

Figure 10. CHFEP's for Ti, Mn, Ni, Cu.

TABLE 24. Effective Potentials for K, Ca, Sc.[22]

	K			Ca			Sc		
	n		A	n		A	n		A
V_{s-d}	-2	0.3538	8.2055	-2	0.3492	2.6173	-2	0.3053	4.9647
	-2	0.0846	0.5086	-2	0.1630	2.3536	-2	0.9310	0.5598
	0	1.0910	-0.7927	0	1.0815	2.4494	0	1.1569	0.7801
V_{p-d}	-2	0.4676	6.8315	-2	0.1850	4.7587	-2	0.2085	4.7923
	0	0.1496	0.2874	0	9.4542	-44.3304	0	0.0340	-20.7844
	0	0.4673	1.1498						
V_d	-1	0.6990	-4.4701	-1	0.2905	- 4.8922	-1	0.2792	- 3.6468
	-1	0.2042	-0.2924	-1	16.3747	- 8.3855	-1	17.2884	- 9.2978
	0	0.3325	-0.1675	0	0.3616	2.4385	0	0.3568	1.7951
	-1	0.0	-1.0	0	3.6467	- 6.7625	0	3.6637	- 9.0138
				-1	0.0	- 2.0	-1	0.0	- 3.0

TABLE 25. Effective Potentials for Ti, V, Cr[22]

	Ti			V			Cr		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.3590	4.9829	-2	0.2842	4.4151	-2	0.3821	5.3702
	-2	0.1103	0.6392	-2	0.1346	1.4886	-2	0.1421	1.1660
	0	1.2504	0.8910	0	0.2837	-0.6754	0	0.3715	-0.7280
V_{p-d}	-2	0.2355	4.8482	-2	0.2533	4.5544	-2	0.2542	3.9379
	0	4.1807	34.6559	0	2.2214	5.9887	0	2.6764	14.9828
V_d	-1	0.2950	- 3.4477	-1	0.3080	- 3.0457	-1	0.3259	- 2.9082
	-1	19.3506	- 9.3647	-1	18.2528	- 9.0515	-1	18.2254	- 8.8759
	0	0.3752	1.7676	0	0.3873	1.5612	0	0.3992	1.5767
	0	4.1458	-10.0024	0	4.1916	-10.0532	0	4.3013	- 9.7391
	-1	0.0	- 4.0	-1	0.0	- 5.0	-1	0.0	- 6.0

TABLE 26. Effective Potentials for Mn, Fe, Co.[22]

	Mn			Fe			Co		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.9166	7.7480	-2	0.9801	7.9679	-2	0.9502	7.6695
	0	0.4794	1.3887	0	0.4995	1.2897	0	0.5022	1.0433
	0	11.0313	-68.2684	0	9.4361	-51.1413	0	9.0267	-36.6976
V_{p-d}	-2	0.3513	5.1042	-2	0.3878	4.4568	-2	0.4182	4.7183
	0	4.5939	23.0171	0	5.9749	31.0750	0	4.0228	16.9933
V_d	-1	0.5586	- 1.5146	-1	0.5906	- 1.3803	-1	0.6175	- 1.2892
	-1	19.6719	- 9.9355	-1	19.8832	- 9.9253	-1	19.9427	- 9.7549
	0	4.4502	-13.0198	0	4.5211	-12.6628	0	4.6595	-12.3436
	-1	0.0	- 7.0	-1	0	- 8.0	-1	0	- 9.0

TABLE 27. Effective Potentials for Ni, Cu, Zn[22]

	Ni			Cu			Zn		
	n	ζ	A	n	ζ	A	n	ζ	A
V_{s-d}	-2	0.9594	7.4654	-2	1.3003	10.0886	-2	1.1822	8.4472
	0	0.5037	0.8480	0	0.5074	0.8710	0	0.5201	0.7141
	0	8.8741	-28.6691	0	8.8578	-74.4868	0	9.8977	-42.0838
V_{p-d}	-2	0.4648	4.8074	-2	0.4105	3.3446	-2	0.5343	4.4655
	0	5.6246	23.6108	0	5.5933	116.6651	0	5.8916	27.2524
V_d	-1	0.6598	- 1.2469	-1	0.6920	- 1.1364	-1	0.6882	- 1.0113
	-1	21.6642	- 9.8266	-1	21.9913	- 9.8189	-1	21.4362	- 9.6752
	0	5.0214	-12.8377	0	5.0409	- 12.6078	0	5.0389	-11.8776
	-1	0[illegible]	-10.0	-1	0.0	- 11.0	-1	0.0	-12.0

TABLE 28. Ca Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Ca $4s^2$	ε_{4s}	- 0.197	-0.196	.001
Singlet	E_T	-676.22511	-0.61531	--
Ca $4s^1 4p^1$	ε_{4s}	- 0.264	-0.265	.001
Triplet	ε_{4p}	- 0.150	-0.152	.002
	E_T	-676.18122	-0.57542	--
	ΔE_T	0.04389	0.03989	.004
Ca $4s^1 4p^1$	ε_{4s}	- 0.237	-0.244	.007
Singlet	ε_{4p}	- 0.082	-0.083	.001
	E_T	-676.11694	-0.50986	--
	ΔE_T	0.10817	0.10545	.003
Ca $4s^1 3d^1$	ε_{4s}	- 0.182	-0.185	.003
Triplet	ε_{3d}	- 0.147	-0.144	.003
	E_T	-676.16243	-0.55375	--
	ΔE_T	0.06268	0.06156	.001
Ca $4s^1 3d^1$	ε_{4s}	- 0.152	-0.149	.003
Singlet	ε_{3d}	- 0.147	-0.143	.004
	E_T	-676.14087	-0.52653	--
	ΔE_T	0.08424	0.08878	.005

TABLE 28 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
Ca^{+1} $4s^1$	ε_{4s}	- 0.421	-0.428	.007
Doublet	E_T	-676.03493	-0.42755	--
	ΔE_T	0.19018	0.18776	.002

TABLE 29. Sc Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Sc $4s^2 3d^1$	ε_{4s}	- 0.208	-0.208	.000
Doublet	ε_{3d}	- 0.344	-0.342	.002
	E_T	-759.70206	-1.57242	--
Sc $4s^1 3d^2$	ε_{4s}	- 0.178	-0.183	.005
Quartet	ε_{3d}	- 0.195	-0.179	.02
	E_T	-759.64580	-1.51751	--
	ΔE_T	0.05626	0.05491	.001
Sc $4s^1 4p^1 3d^1$	ε_{4s}	- 0.281	-0.286	.005
Quartet	ε_{3d}	- 0.380	-0.384	.004
	ε_{4p}	- 0.158	-0.163	.005
	E_T	-759.66029	-1.54019	--
	ΔE_T	0.04177	0.03223	.01
Sc^{+1} $4s^1 3d^1$	ε_{4s}	- 0.448	-0.460	.01
Triplet	ε_{3d}	- 0.600	-0.606	.006
	E_T	-759.50642	-1.38186	--
	ΔE_T	0.19564	0.19056	.005
Sc^{+1} $4s^2$	ε_{4s}	- 0.488	-0.499	.01
Singlet	E_T	-759.42857	-1.28713	--
	ΔE_T	0.27349	0.28529	.01
Sc^{+1} $3d^2$	ε_{4s}	- 0.442	-0.431	.01
Triplet	E_T	-759.46876	-1.33549	--
	ΔE_T	0.23330	0.23693	.004

TABLE 29 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
Sc^{+2} $3d^1$	ε_{3d}	- 0.904	-0.923	.02
Doublet	E_T	-758.06048	-0.92314	--
	ΔE_T	0.64158	0.64928	.008
Sc^{+2} $4s^1$	ε_{4s}	- 0.762	-0.793	.03
Doublet	E_T	-758.94493	-0.79320	--
	ΔE_T	0.75713	0.81529	.06

TABLE 30. Ti Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Ti $4s^2 3d^2$	ε_{4s}	- 0.218	-0.219	.001
Triplet	ε_{3d}	- 0.438	-0.434	.004
	E_T	-848.36408	-3.37018	--
Ti $4s^2 3d^2$	ε_{4s}	- 0.220	-0.219	.001
Singlet	ε_{3d}	- 0.378	-0.376	.002
	E_T	-848.30326	-3.30959	--
	ΔE_T	0.06082	0.06059	.0002
Ti $4s^1 3d^3$	ε_{4s}	- 0.188	-0.195	.007
Triplet	ε_{3d}	- 0.242	-0.227	.02
	E_T	-848.32167	-3.33208	--
	ΔE_T	0.04241	0.03810	.004
Ti $4s^1 4p^1 3d^2$	ε_{4s}	- 0.298	-0.309	.01
Triplet	ε_{3d}	- 0.473	-0.482	.01
	ε_{4p}	- 0.167	-0.165	.002
	E_T	-848.32477	-3.33717	--
	ΔE_T	0.03931	0.03301	.006
Ti^{+1} $4s^1 3d^2$	ε_{4s}	- 0.473	-0.490	.02
Doublet	ε_{3d}	- 0.705	-0.707	.002
	E_T	-848.16264	-3.17730	--
	ΔE_T	0.20144	0.19288	.009
Ti^{+1} $4s^2 3d^1$	ε_{4s}	- 0.512	-0.522	.01
Doublet	ε_{3d}	- 0.900	-0.933	.03
	E_T	-848.01543	-3.01288	--
	ΔE_T	0.34864	0.35730	.009

TABLE 30 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
Ti^{+1} $3d^3$	ε_{3d}	- 0.504	- .497	.007
Quartet	E_T	-848.13518	-3.13804	--
	ΔE_T	0.22890	0.23214	.003
Ti^{+2} $3d^2$	ε_{3d}	- 1.023	-1.038	.02
Triplet	E_T	-847.69154	-2.68955	--
	ΔE_T	0.67254	0.68063	.008
Ti^{+2} $4s^1 3d^1$	ε_{4s}	- 0.804	-0.837	.03
Triplet	ε_{3d}	- 1.235	-1.287	.05
	E_T	-847.51270	-2.50566	--
	ΔE_T	0.85138	0.86452	.01

TABLE 31. V Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
V $4s^2 3d^3$	ε_{4s}	- 0.228	-0.228	.000
Quartet	ε_{3d}	- 0.503	-0.502	.001
	E_T	-942.83485	-6.14401	--
V $4s^1 3d^4$	ε_{4s}	- 0.196	-0.206	.01
Sextet	ε_{3d}	- 0.263	-0.249	.01
	E_T	-942.80423	-6.12117	--
	ΔE_T	0.0306	0.0228	.007
V $3d^5$	ε_{3d}	- 0.061	-0.061	.000
Sextet	E_T	-942.61667	-5.92412	--
	ΔE_T	0.2182	0.2207	.003
V $4s^1 4p^1 3d^3$	ε_{4s}	- 0.314	-0.327	.01
Sextet	ε_{3d}	- 0.546	-0.546	.000
	ε_{4p}	- 0.171	-0.169	.002
	E_T	-942.79513	-6.11378	--
	ΔE_T	0.0397	0.0302	.009
V^{+1} $4s^2 3d^2$	ε_{4s}	- 0.534	-0.543	.009
Triplet	ε_{3d}	- 1.020	-1.050	.03
	E_T	-942.45103	-5.75215	--
	ΔE_T	0.3838	0.3919	.008
V^{+1} $4s^1 3d^3$	ε_{4s}	- 0.491	-0.517	.03
Quintet	ε_{3d}	- 0.781	-0.784	.003
	E_T	-942.62829	-5.94954	--
	ΔE_T	0.2066	0.1945	.01

TABLE 31 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
V^{+1} $3d^4$	ε_{3d}	- 0.537	-0.533	.004
Quintet	E_T	-942.60912	-5.91671	--
	ΔE_T	0.2257	0.2281	.002
V^{+2} $4s^1 3d^2$	ε_{4s}	- 0.842	-0.878	.04
Quartet	ε_{3d}	- 1.368	-1.415	.05
	E_T	-941.93104	-5.23303	--
	ΔE_T	0.9038	0.9110	.007
V^{+2} $3d^3$	ε_{3d}	- 1.113	-1.129	.02
Quartet	E_T	-942.13388	-5.43515	--
	ΔE_T	0.7010	0.7096	.009

TABLE 32. Cr Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Cr $4s^1 3d^5$	ε_{4s}	- 0.204	- 0.205	.001
Heptet	ε_{3d}	- 0.332	- 0.312	.02
	E_T	-1043.26492	-10.01801	--
Cr $4s^2 3d^4$	ε_{4s}	- 0.237	- 0.228	.009
Quintet	ε_{3d}	- 0.537	- 0.540	.003
	E_T	-1043.24600	- 9.99099	--
	ΔE_T	0.01892	0.02702	.008
Cr $3d^6$	ε_{3d}	- 0.098	- 0.078	.02
Quintet	E_T	-1042.91191	- 9.65260	--
	ΔE_T	0.35311	0.36580	.01
Cr $4p^1 3d^5$	ε_{3d}	- 0.398	- 0.381	.02
Heptet	ε_{4p}	- 0.112	- 0.113	.001
	E_T	-1043.17394	- 9.9264	--
	ΔE_T	0.09098	0.09200	.001
Cr^{+1} $4s^2 3d^3$	ε_{4s}	- 0.554	- 0.548	.006
Quartet	ε_{3d}	- 1.110	- 1.144	.03
	E_T	-1042.82924	- 9.56355	--
	ΔE_T	0.43568	0.45446	.02
Cr^{+1} $4s^1 3d^4$	ε_{4s}	- 0.519	- 0.525	.006
Sextet	ε_{3d}	- 0.825	- 0.824	.001
	E_T	-1043.03481	- 9.79914	--
	ΔE_T	0.23011	0.21887	.01

TABLE 32 Continued.

State/Coupling		Full SCF	Eff. Pot.	Error
Cr^{+1} $3d^5$	ε_{3d}	$-$ 0.618	-0.603	.02
Sextet	E_T	-1043.06212	-9.81383	--
	ΔE_T	0.20280	0.20418	.001
Cr^{+2} $4s^1 3d^3$	ε_{4s}	$-$ 0.878	-0.894	.02
Quintet	ε_{3d}	$-$ 1.470	-1.512	.04
	E_T	-1042.29299	-9.04440	--
	ΔE_T	0.97099	0.97361	.003
Cr^{+2} $3d^4$	ε_{3d}	$-$ 1.170	-1.176	.006
Quintet	E_T	-1042.51832	-9.27620	--
	ΔE_T	0.74657	0.74223	.004

TABLE 33. Mn Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Mn $4s^2 3d^5$	ε_{4s}	- 0.245	- 0.244	.001
Sextet	ε_{3d}	- 0.628	- 0.627	.001
	E_T	-1149.78740	-15.21117	--
Mn $4s^1 3d^6$	ε_{4s}	- 0.207	- 0.215	.008
Sextet	ε_{3d}	- 0.357	- 0.347	.01
	E_T	-1149.62856	-15.06271	--
	ΔE_T	0.15884	0.14846	.01
Mn $3d^7$	ε_{3d}	- 0.087	- 0.085	.002
Quartet	E_T	-1149.30734	-14.73980	--
	ΔE_T	0.48006	0.47137	.01
Mn $4s^1 4p^1 3d^5$	ε_{4s}	- 0.342	- 0.361	.02
Octet	ε_{4p}	- 0.179	- 0.176	.003
	ε_{3d}	- 0.666	- 0.669	.003
	E_T	-1149.74638	-15.18506	--
	ΔE_T	0.04102	0.02611	.02
Mn^{+1} $4s^1 3d^5$	ε_{4s}	- 0.539	- 0.566	.03
Heptet	ε_{3d}	- 0.925	- 0.927	.002
	E_T	-1149.57207	-15.01377	--
	ΔE_T	0.21533	0.19740	.02
Mn^{+1} $3d^6$	ε_{3d}	- 0.652	- 0.652	.001
Quintet	E_T	-1149.42283	-14.84861	--
	ΔE_T	0.36457	0.36256	.002
Mn^{+1} $4s^2 3d^4$	ε_{4s}	- 0.574	- 0.582	.008
Quintet	ε_{3d}	- 1.216	- 1.241	.03
	E_T	-1149.29416	-14.71072	--
	ΔE_T	0.49324	0.50045	.007

TABLE 33 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
Mn^{+1} $3d^5$ Sextet	3d	- 1.284	- 1.299	.02
	E_T	-1149.03503	-14.45092	--
	E_T	0.75237	0.76025	.008

TABLE 34. Co Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Co $4s^2 3d^7$	ε_{4s}	- 0.263	- 0.263	.000
Quartet	ε_{3d}	- 0.616	- 0.614	.002
	E_T	-1381.29988	-29.50895	--
Co $4s^1 3d^8$	ε_{4s}	- 0.214	- 0.218	.004
Quartet	ε_{3d}	- 0.348	- 0.342	.006
	E_T	-1381.20349	-29.41772	---
	ΔE_T	0.09649	0.09123	.005
Co $3d^9$	ε_{3d}	- 0.068	- 0.069	.001
Doublet	E_T	-1380.88692	-29.10359	--
	ΔE_T	0.41306	0.40536	.008
Co $4p^1 3d^8$	ε_{4p}	- 0.113	- 0.114	.001
Quartet	ε_{3d}	- 0.426	- 0.427	.001
	E_T	-1381.10303	-29.31405	--
	ΔE_T	0.19695	0.19490	.002
Co^{+1} $4s^1 3d^7$	ε_{4s}	- 0.568	- 0.587	.02
Quintet	ε_{3d}	- 0.931	- 0.932	.001
	E_T	-1381.05908	-29.27848	.01
Co^{+1} $3d^8$	ε_{3d}	- 0.661	- 0.664	.003
Triplet	E_T	-1380.98999	-29.20002	--
	ΔE_T	0.30999	0.30893	. 01
Co^{+1} $4s^2 3d^6$	ε_{4s}	- 0.613	- 0.621	.008
Quintet	ε_{3d}	- 1.191	- 1.206	.02
	E_T	-1380.90307	-29.10926	--
	ΔE_T	0.39691	0.39969	.0002

TABLE 34 Continued

State/Coupling		Full SCF	Eff. Pot.	Error
Co^{+2} 3d^{7}	ε_{3d}	- 1.316	- 1.330	.01
Quartet	E_T	-1380.49332	-28.69366	--
	ΔE_T	0.80666	0.81529	.008
Co^{+3} 3d^{6}	ε_{3d}	- 2.006	- 2.048	.04
Quintet	E_T	-1379.34173	-27.51773	--
	ΔE_T	1.95825	1.99122	.03

TABLE 35. Cu Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Cu $4s^1 3d^{10}$	ε_{4s}	- 0.22918	- 0.22957	.0004
Doublet	ε_{3d}	- 0.46044	- 0.46145	.0001
	E_T	-1638.80673	-50.69719	--
Cu $4p^1 3d^{10}$ Doublet	ε_{4p_x}	- 0.11653	- 0.11665	.0001
	εd_{z^2}	- 0.54425	- 0.54852	.004
	E_T	-1638.69498	-50.58495	--
	ΔE_T	0.11174	0.11223	.001
Cu $4s^2 3d^9$	ε_{4s}	- 0.28306	- 0.28152	.002
Doublet	ε_{3d^1}	- 0.83326	- 0.84104	.009
	ε_{3d^2}	- 0.75138	- 0.75837	.007
	E_T	-1638.80610	-50.69201	--
	ΔE_T	- 0.00027	0.0052	.0054
Cu^{+1} $4s^1 3d^9$	ε_{4s}	- 0.59826	- 0.60691	.009
Triplet	ε_{3d^2}	- 1.09102	- 1.10079	.01
	ε_{3d^1}	- 1.17499	- 1.18724	.01
	E_T	-1638.53760	-50.42724	--
	ΔE_T	0.26912	0.26995	.0008
Cu^{+1} $3d^{10}$	ε_{3d}	- 0.78921	- 0.79435	.005
Singlet	E_T	-1638.57854	-50.46837	--
	ΔE_T	0.22819	0.22882	.0006
Cu^{+2} $3d^9$	ε_{3d^1}	- 1.57043	- 1.5887	.02
Doublet	ε_{3d^2}	- 1.45452	- 1.4717	.02
	E_T	-1637.94136	-49.82229	--
	ΔE_T	0.86536	0.87490	.01

TABLE 36. Zn Tests[21], Energies in Hartrees.

State/Coupling		Full SCF	Eff. Pot.	Error
Zn $4s^2 3d^{10}$	ε_{4s}	- 0.286	- 0.286	.000
Singlet	ε_{3d}	- 0.755	- 0.754	.001
	E_T	-1777.67477	-63.89602	--
Zn $4s^1 4p^1 3d^{10}$	ε_{4s}	- 0.386	- 0.390	.004
Triplet	ε_{3d}	- 0.826	- 0.826	.000
	ε_{4p}	- 0.185	- 0.184	.001
	E_T	-1777.57980	-63.80177	--
	ΔE_T	0.09497	0.09425	.0007
Zn^{+1} $4s^1 3d^{10}$	ε_{4s}	- 0.604	- 0.614	.01
Doublet	ε_{3d}	- 1.102	- 1.105	.003
	E_T	-1777.39988	-63.62244	--
	ΔE_T	0.27489	0.27358	.001
Zn^{+1} $4s^2 3d^9$	ε_{4s}	- 0.669	- 0.676	.007
Doublet	ε_{3d}	- 1.416	- 1.430	.01
	E_T	-1777.12848	-63.34657	--
	ΔE_T	0.54629	0.54945	.003
Zn^{+2} $3d^{10}$	ε_{3d}	- 1.520	- 1.533	.01
Singlet	E_T	-1776.79711	-63.00994	--
	ΔE_T	0.87766	0.88608	.008

TABLE 36 Continued.

State/Coupling		Full SCF	Eff. Pot.	Error
Zn^{+2} $4s^1 3d^9$	ε_{4s}	- 1.048	- 1.071	.02
Triplet	ε_{3d}	- 1.843	- 1.865	.02
	E_T	-1776.47022	-62.68567	--
	ΔE_T	1.20455	1.21035	.006

TABLE 37. Exponents for Three Term Gaussian Basis 4s Coreless Hartree-Fock Orbitals. K through Zn.

K	Ca	Sc	Ti
0.270275	0.44883	0.63200	0.6780
0.040528	0.06209	0.03132	0.0651
0.018283	0.02504	0.02834	0.0209

V	Cr	Mn	Fe
0.75580	0.76559	0.87877	0.97543
0.07336	0.07017	0.08105	0.08824
0.02590	0.02638	0.01339	0.01504

CO	Ni	Cu	Zn
1.08436	1.1760	1.0720	1.25022
0.09910	0.1110	0.0995	0.13642
0.03285	0.0393	0.0357	0.04718

TABLE 38. Small Basis Set Calculations for Ti and Cu, Energies in Hartrees.

State/Coupling		Large Basis	Small Basis[+]	Error
Ti $4s^2 3d^2$ Triplet	ε_{4s}	-0.218	-0.219	.001
	ε_{3d}	-0.437	-0.434	.003
	E_T	-3.36629	-3.36976	.003
Cu $4s^1 3d^{10}$ Doublet	ε_{4s}	-0.22928	-0.22969	.0004
	ε_{3d}	-0.45950	-0.46391	.005
	E_T	-50.69719	-50.69714	.00005

[+] Using the 3s type functions of Table 37 with the 5d type functions of Wachters[24] contracted (1,1,1/5).

D. Cu One Electron CHFEP

The effective potentials we have developed until this point were based on the usual core-valence separation of orbitals. We know however that in some cases, orbitals that are usually classified as valence orbitals, can be considered core orbitals. Mary-Beth Baillie et al.[25,26,27] have found for example that for Cu in Cu_2, CuH and Cu_2H_2, the d orbitals of Cu do not undergo any significant change upon molecular formation. It would then be an additional savings in computational effort if the d orbitals were incorporated into the effective potential. This one electron potential along with some tests are presented in Tables 39 and 40 respectively. Included in Table 39 is the Ni one electron effective potential developed by Carl F. Melius. Mary-Beth Baillie, *et al.*[25,26,27] have found that for Cu_2, CuH and Cu_2H_2 this one electron effective potential reproduces the results of more elaborate calculations quite well.

TABLE 39. Ni and Cu One Electron Effective Potential[22]

Ni

	n	ζ	A
V_s	-2	1.17326	2.60210
	0	0.12656	- 0.06672
V_d	-2	0.01299	0.15429
	-1	0.0	- 1.0
V_{p-d}	-2	1.08491	1.79801
	0	0.06158	- 0.01714

Cu

	n	ζ	A
V_{s-d}	-2	1.15858	2.96371
	0	0.25712	- 0.19867
V_d	-2	0.03588	0.14945
	-1	0.0	- 1.0
V_{p-d}	-2	3.59990	12.44478
	0	0.12943	- 0.05452

TABLE 40. Cu One Electron Effective Potential Tests, Energies in Hartrees.

	ε_{4s}	Error	ε_{4p}	Error
Full Basis without Potential	-0.22940	--	-0.12087	--
Full Basis with 11 Electron Potential	-0.22857	.0008	-0.12049	.0004
Full Basis with 1 Electron Potential	-0.22866	.0007	-0.12053	.0003
Three Term Basis[+] with 11 Electron Potential	-0.22969	.0003		
Three Term Basis[+] with 1 Electron Potential	-0.22850	.0009		

[+] Using the basis set given in Table 37.

V. CONCLUSION

The effective potentials that have been presented and tested here, appear to provide a promising approach to SCF calculations. The essential features of complete SCF calculations are reproduced quite accurately. The agreement between the effective potential SCF calculations and complete SCF calculations for various excited states show that the underlying approximation of the frozen core does not introduce any serious error.

In addition, by reducing the basis sets to a size needed by just the valence pseudoorbitals, we are able to greatly reduce the time and cost of SCF calculations. It appears to be worthwhile to continue the development of CHFEP's for the second and third row transition elements. No great difficulty is forseen in doing so.

REFERENCES

1. J. D. Weeks, A. Hazi, and S. A. Rice, Advan. Chem. Phys. 16, 283 (1969).

2. J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

3. H. Hellmann, Acta Fizichim., USSR, 1, 913 (1935).

4. P. Gombas, Z. Phys., 118, 164 (1941).

5a. L. Szasz and G. McGinn, J. Chem. Phys. 42, 2363 (1965).

b. L. Szasz and G. McGinn, J. Chem. Phys. 45, 2898 (1966).

6. G. Simons and A. Mazziotti, J. Chem. Phys. 52, 2449 (1970).

7. I. V. Abarenkov and V. Heine, Phil. Mag. 12, 529 (1965).

8. G. Simons, J. Chem. Phys. 55, 756 (1971).

9a. P. L. Goodfriend and G. A. Hart, J. Molec. Spectros. 42, 312 (1972).

b. G. A. Hart and P. L. Goodfriend, Molec. Phys. 29, 1109 (1975)

10a. E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2637 (1963).

b. E. Clementi, D. L. Raimondi, and W. P. Reinhardt, J. Chem. Phys. 47, 1300 (1967).

11a. M. E. Schwartz and J. D. Switalski, J. Chem. Phys. 57, 4125 (1972).

b. M. E. Schwartz and J. D. Switalski, J. Chem. Phys. 57, 4132 (1972).

12. T. C. Chang, P. Habitz, B. Pittel, and W. H. E. Schwartz, Theoret. Chim. Acta (Berl.) 34, 263 (1974).

13. P. Coffey, C. S. Ewig and J. R. Van Wazer, J. Am. Chem. Soc. 97, 1656 (1975).

14. V. Bonifacic and S. Huzinaga, J. Chem. Phys. 60, 2779 (1974).

15. P. Durand and J. C. Barthelat, Theoret. Chim. Acta (Berl.) 38, 283 (1975).

16. L. R. Kahn and W. A. Goddard III, J. Chem. Phys. 56, 2685 (1972).

17. C. F. Melius, Ph.D. Thesis (California Institute of Technology, 1972) (unpublished).

18. C. F. Melius, W. A. Goddard III, and L. R. Kahn, J. Chem. Phys. 56, 3342 (1972); C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3348 (1972); Phys. Rev. A, 10, 1528 (1974); C. F. Melius, B. D. Olafson and W. A. Goddard III, Chem. Phys. Letters 28, 457 (1974).

19. The present work was done in collaboration with C. F. Melius. The programs used to form the effective potentials and small basis sets were developed by him, as were the necessary modifications to the "Polyatom" system of programs, to include these effective potentials. Many of the potentials were developed by C. F. Melius and are presented here for the sake of completeness. In addition much of the testing was done by him.

20. W. J. Hunt, P. J. Hay and W. A. Goddard III, J. Chem. Phys. 57, 738 (1972).

21. The program used in testing these potentials was part of the Generalized Valence Bond (GVB) system of programs[20] which was used here to perform Orthogonality Constrained Basis Set Expansion Method (OCBSE)[28] type calculations. This program does not easily handle pure states. Since the purpose of these tests was to compare the results of calculations with the effective potentials to those without, many of the tests presented are for states which are mixtures of different L and different S values. For example in Table 9 for oxygen, the ground state given is for the occupancy $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. This results in different values for ε_x and ε_y. For this reason we present an ε_{2p^2} for the doubly occupied $2p_x$ orbital and a different ε_{2p^1} for the singly occupied $2p_y$ and $2p_z$ orbitals. Similarly, for the transition elements many of the d orbitals with different spatial symmetry (dxy, dxz, dyz, $d_{x^2-y^2}$, d_{z^2}) have different orbital energies. For those cases we present only one each of a singly occupied, and a doubly occupied orbitals, or just one sample d orbital energy.

22. The effective potentials presented in these tables (W^{EP}) are for the effective Hamiltonians

$$H^{EP} = T + W^{EP} + V_{\chi_v} = T - \frac{n_v}{r} + V^{EP} + V_{\chi_v}$$

where V_{χ_v} represents the appropriate coulomb and exchange operators for the valence orbitals, n_v is the number of valence orbitals and W^{EP} is of the form

$$W^{EP} = W_{LMAX}(r) + \sum_{\ell=0}^{LMAX-1} \sum_m W_\ell(r)\,|\ell m\rangle\langle \ell m|$$

and where $W(r)$ $(= W_{LMAX}(r)$ or $W_\ell(r))$ is given by

$$W(r) = \sum_i A_i\, r^{n_i}\, e^{-\alpha_i r^2}.$$

23. T. H. Dunning. Private communication.

24. A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1970).

25. Mary-Beth Baillie, Ph.D. Thesis (New York University, 1976) (unpublished).

26. Mary-Beth Baillie, Jules W. Moskowitz, Carl F. Melius, Mark Ratner, Al Mortola, to be published, Surface Science.

27. W. J. Hunt, T. H. Dunning Jr. and W. A. Goddard III, Chem. Phys. Lett. 3, 606 (1969).

28. S. Huzinaga and Y. Sakai, J. Chem. Phys. 50, 1371 (1969).

29. Sid Topiol, Ph.D. Thesis (New York University) (unpublished).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Administration, nor any person acting on behalf of the Administration:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Administration" includes any employee or contractor of the Administration, or employee of such contractor, to the extent that such employee or contractor of the Administration, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Administration, or his employment with such contractor.

NEW YORK UNIVERSITY
COURANT INSTITUTE-LIBRARY

NYU
COO-
3077-105 c.1

Topiol
Ab initio effective potentials
for atoms of the first three
rows of the periodic table.

N.Y.U. Courant Institute of
Mathematical Sciences
251 Mercer St.
New York, N. Y. 10012